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At-Sea Incineration of Herbicide Orange Onboard the M/T Vulcanus

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AT-SEA INCINERATION OF HERBICIDE ORANGE ONBOARD THE M/T VULCANUS

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16. ABSTRACT The report describes the at-sea incineration of three shiploads (approximately 10,400 metric tons) of U.S. Air Force-owned Herbicide Orange onboard the incinerator ship M/T Vulcanus, within an EPA-designated Pacific Ocean burn zone, west of Johnston Atoll. The first shipload, transported to the burn zone from the U.S. Naval Construction Battalion Base, Gulfport, Mississippi, was incinerated under EPA research permit. Shiploads 2 and 3 were taken onboard M/T Vulcanus at Johnston Island and incinerated under EPA special permit. The incineration was monitored, sampled, and analyzed to ensure compliance with EPA permit operating and safety conditions related to at-sea operations. An EPA representative was onboard M/T Vulcanus during the initial burn. A U.S. Air Force representative participated in monitoring all three burns. Monitoring utilized on-line instrumentation to measure CO and CO2, oxygen concentration, and total hydrocarbons from both incinerators. These parameters served as a measure of overall combustion efficiency with primary emphasis on the CO2/CO ratio in the effluent gases. Combustion efficiency exceeded 99.9% during all three burns. Destruction and combustion efficiencies measured during all burns met or exceeded requirements. All other conditions of the permits related to at-sea incineration operations were met.

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Incinerators	Carbon Dioxide	At-Sea Incineration		
Herbicides	Hydrocarbons	Herbicide Orange	06F	07C
Waste Disposal	Oxygen	Dioxin		
Ships	Butyl Acetates		13J	
Sea Water			08J	

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by

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ABSTRACT

This report describes at-sea incineration of approximately 10,400 metric tons of U.S. Air Force-owned Herbicide Orange onboard the incinerator ship M/T Vulcanus. Incineration took place within a Pacific Ocean burn zone located West of Johnston Atoll which was designated by the U.S. Environmental Protection Agency. Three shiploads of Herbicide Orange were incinerated. The first shipload was transported from the U.S. Naval Construction Battalion Base at Gulfport, Mississippi, to the burn zone and incinerated under provisions of U.S. EPA Research Permit No. 770DH001R. Shiploads two and three were subsequently taken onboard the Vulcanus at Johnston Island and incinerated under U.S. EPA Special Permit No. 770DH001S. The U.S. Air Force and Ocean Combustion Services, B.V., The Netherlands (owner of the M/T Vulcanus), were the permittees.

Monitoring, sampling, and analysis of the incineration process to assure compliance with U.S. EPA permit operating and safety conditions related to at-sea operations were performed by personnel of TRW, Inc., Redondo Beach, California. A U.S. EPA representative was onboard the Vulcanus during the Research Permit burn. A U.S. Air Force representative participated in the monitoring team activities during all three burns.

Monitoring activities utilized on-line instrumentation to measure carbon monoxide and dioxide, oxygen concentration, and total hydrocarbons from both incinerators. These parameters served as a measure of overall combustion efficiency with primary emphasis on the ratio of carbon dioxide to carbon monoxide in the effluent gases. Combustion efficiency exceeded 99.9% during all three burns. Herbicide Orange was injected into the incineration system at an average rate of 14.5 metric tons per hour. Optical pyrometer flame temperature measurements averaged 1500°C. A dwell time of 1.0 second was calculated for the combustion gases in the incinerators.

Effluent sampling was accomplished using a traversing sample probe installed on the starboard incinerator. A USAF benzene impinger train and a modified EPA Method 5 train were used to acquire combustion effluent samples. Analysis of these samples was conducted to determine destruction efficiencies for the normal butyl esters of 2,4-dichlorophenoxyacetic acid and 2,4,5 trichlorophenoxyacetic acid, primary constituents of Herbicide Orange, as well as 2,3,7,8 tetrachlorodibenzo-p-dioxin, a contaminant present in the herbicide. Destruction efficiencies in excess of 99.9% were determined for all three burns.

Destruction and combustion efficiencies measured during the Research and Special Permit burns met or exceeded requirements. All other conditions of the permits related to at-sea incineration operations were met including adherence to a comprehensive safety plan.

This report was submitted in fulfillment of Contract No. 68-01-2966 by TRW Defense and Space Systems Group, TRW Inc., under sponsorship of the U.S. Environmental Protection Agency. This report covers the period 15 April 1977 to 15 April 1978.

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Technical direction, assistance, and planning of the conceptual design and implementation of this program were received from a number of agencies and organizations within the U.S. Government. These include the U.S. Environmental Protection Agency's Oil and Special Materials Control Division (OSMCD), Washington, D.C., Industrial Environmental Research Laboratory (IERL), Research Triangle Park, North Carolina, and the Regional Office, Region IX, San Francisco, California; the U.S. Air Force's Occupational and Environmental Health Laboratories (OEHL), Kelly and Brooks Air Force Bases, Texas, and McClellan Air Force Base, California; the Air Force Logistics Command, Wright-Patterson Air Force Base, Dayton, Ohio; the Military Sealift Command; the Military Airlift Command; and the Defense Nuclear Agency. The Honolulu, Hawaii, Communications Station of the U.S. Coast Guard provided communications between the M/T Vulcanus and Johnston Island. U.S. Coast Guard Headquarters, Washington, D.C., provided guidance in installation of equipment on the Vulcanus to conform with U.S. maritime regulations.

The authors are indebted to the many individuals of all of these organizations for their contributions.

1. INTRODUCTION, BACKGROUND, AND SUMMARY

1.1 INTRODUCTION

Thermal destruction of combustible wastes at sea is recognized as an alternative to land based incineration. In late 1974 and in March of 1977, organochlorine wastes were incinerated in the Gulf of Mexico by the Motor Tanker (M/T) Vulcanus. These efforts, evaluated by the U.S. Environmental Protection Agency (U.S. EPA), provided a technical basis for concluding that at-sea incineration is a viable alternative to other means of disposal.

Incineration of U.S. Air Force stocks of Herbicide Orange was performed onboard the M/T Vulcanus operating in the Pacific Ocean west of Johnston Atoll. Approximately 10,400 metric tons were incinerated under permits granted by the U.S. EPA. The first shipload, loaded at the Naval Construction Battalion Center at Gulfport, Mississippi, was incinerated under Research Permit No. 770DH001R. The second and third shiploads, loaded at Johnston Island (one of the islands comprising Johnston Atoll), were incinerated under Special Permit No. 770DH001S.

The Herbicide Orange incinerated consisted of an approximate 50-50 mixture by volume of the n-butyl esters of 2,4-dichlorophenoxyacetic acid (2,4-D) and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T)(1). There was a small quantity of Orange II herbicide which consisted of an approximate 50-50 mixture by volume of 2,4-D and the iso-octyl ester of 2,4,5-trichlorophenoxyacetic acid(1). Certain lots of the herbicide contained the contaminant 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD). The TCDD concentration in the entire stock of herbicide averaged 1.9 ppm and ranged from 0 to 47 ppm(1). Diesel fuel used to rinse herbicide drums and equipment associated with dedrumming and loading was mixed with the herbicide for incineration.

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1. From U.S. EPA Special Permit No. 770DH001S.

1.2 BACKGROUND

The at-sea incineration of U.S. Air Force stocks of Herbicide Orange was a complex undertaking. A large number of U.S. Government organizations and civilian contractors contributed to the effort, and a brief discussion of the program organization will be helpful in understanding the scope of this report.

Permits to incinerate the waste were granted to the U.S. Air Force, owner of the waste, and to Ocean Combustion Services, B.V., of The Netherlands, owner of the M/T Vulcanus, as co-permittees.

The U.S. EPA contracted with TRW, Inc., to perform environmental monitoring during the incineration of the herbicide. This program was funded by the U.S. Air Force. The scope of TRW's activities under this contract included design and preparation of stack sampling and monitoring equipment, development of a comprehensive personnel protection plan, development and implementation of a sampling and analysis protocol, acquisition of samples and monitoring of combustion effluent during incinerator operation, analysis of the samples and monitoring data, and evaluation of the results.

TRW's role in the incineration program was thus limited to at-sea operations. It was TRW's responsibility to monitor the following permit conditions (renumbered but verbatim from Reference 1):

1. The Permittees are authorized to heat up incinerators with fuel oil while in route to the site but may not incinerate the described wastes except in the site which is defined in longitude and latitude as follows: From 15 degrees 45 minutes to 17 degrees 45 minutes north latitude. From 171 degrees 30 minutes to 173 degrees 30 minutes west longitude.

2. During start-up, Herbicide Orange shall not be fed into the incinerators until a flame temperature of 1280°C has been reached in the furnace and only one burner at a time shall be changed over to the waste. The start-up temperature of 1280°C must be reached before the next burner is changed over to Herbicide Orange.

3. Monitoring of the furnaces for temperature, and for completeness of combustion, shall be in effect during the change-over. A record of temperature shall also be maintained during this time.

4. The incinerator flame temperature shall be greater than 1250°C when burning waste.

5. An automatic shut-off device shall be in operation on both furnaces, set to turn off the flow of waste if the flame temperature drops below 1250°C.

6. The Herbicide Orange feed rate to each incinerator shall not exceed 11.5 tonnes/hour (11.5 metric tons/hour).

7. Incineration shall take place in the presence of excess air such that there shall be a 3 mole percent minimum oxygen content in the combustion product gas.

8. The combustion efficiency of the incineration and destruction efficiency of waste during the incineration will be at least 99.9 percent complete. If the efficiency level falls below 99.9 percent, the incinerators on the Vulcanus will be shut down immediately until corrective measures which assure 99.9 percent combustion efficiency are applied.

9. The emission rates of TCDD, 2,4-D, or 2,4,5-T will not be in excess of 0.1% of the total amounts of TCDD, 2,4-D or 2,4,5-T in the Herbicide Orange waste. (Wright State University had responsibility for analyses to determine emission rates of (TCDD.)

10.a. An automatic sealed monitoring device (black box) will be installed to record incineration activities and temperatures and camera to photograph the control panel every 15 minutes.

10.b. A manual log shall be kept and the following information recorded at 1-hour intervals:

   a. Time, date
   b. "Black box" temperature
   c. Controller temperature reading
   d. Waste feed rates
   e. Switching of waste tanks
   f. Wind speed and direction
   g. Location

   (For the third burn, this requirement was changed to 2-hour intervals.)

11. A device for addition of ammonia to make a visible plume will be installed.

12. Permittees shall ensure their position during transport and within the discharge site at all times by on-board navigational aids, and shall maintain documentation of position.

13. Permittees shall have installed and in operating condition a radio or other communications devices which are capable of voice transmission to the mainland from the Vulcanus when in route to the incineration site and during the incineration of the waste in the designated site. The frequency of reporting and information to be transmitted is set forth in the Herbicide Orange Contingency Plan contained in Appendix 9 of the hearing record of April 7, 1977.

14. During the burns the Permittees shall transmit the following information to EPA Headquarters every 24 hours:

    a. Operating temperatures

    b. Average combustion efficiency

    c. Significant malfunctions/incidents

15. The Permittees shall monitor for carbon monoxide, carbon dioxide, oxygen, 2,4-D, 2,4,5-T, TCDD and other parameters in accordance with the monitoring plan contained in Appendix B (of the permit).

16. The Permittees shall comply with all provisions of the comprehensive safety plan set forth in Appendix C (of the permit).

During incineration of the first shipload, a U.S. EPA Representative was onboard to determine compliance with permit conditions. During incineration of the second and third shiploads, the leader of the TRW sampling team was designated U.S. EPA Advisor relative to permit compliance.

The U.S. Air Force issued a contract (No. F41608-77-C-0169) to the Brehm Laboratory of Wright State University (WSU) to perform analyses for the toxic contaminant (2,3,7,8-tetrachlorodibenzo-p-dioxin, TCDD) in the combustion effluent samples taken onboard the ship during incineration. The analyses by Wright State were intended to determine compliance with the permit requirement that emissions of TCDD not exceed 0.1% of the total TCDD in the waste. In other words, the destruction efficiency of TCDD was required to be not less than 99.9%.

The U.S. Air Force issued a contract (No. F08635-76-D-0168) to Battelle-Columbus Laboratories (BCL) to perform land based environmental monitoring (air, land, and water) during the dedrumming and loading operations at Johnston Atoll. BCL also analyzed combustion effluent, potable water, and workspace air monitor samples from the ship for 2,4-D and 2,4,5-T.

U.S. Air Force Occupational and Environmental Health Laboratories (OEHL) at Kelly and Brooks Air Force Bases, Texas, analyzed miscellaneous samples from both land based and at-sea operations. BCL and WSU analyzed a variety of samples intended to determine the effect of U.S. EPA approved ship cleaning procedures after waste incineration had been completed. The TRW sampling team leader had been designated by the U.S. EPA to monitor that portion of the ship cleaning performed while the TRW team was still onboard the ship.

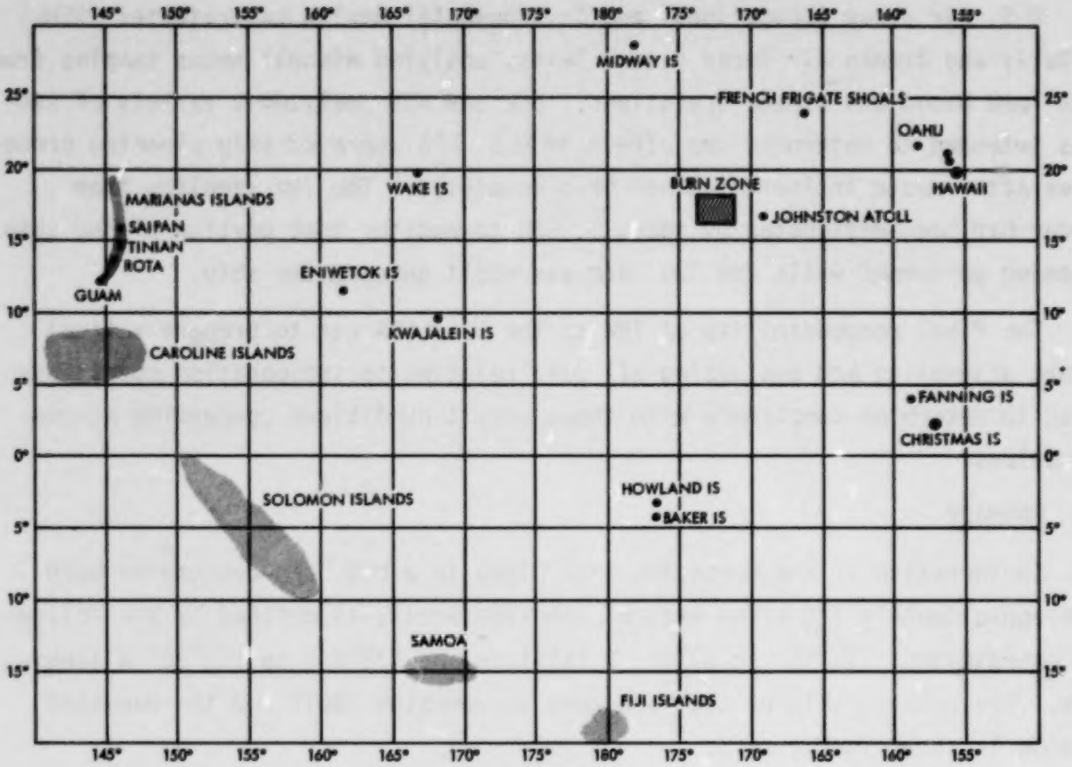
The final responsibility of TRW to the U.S. EPA was to prepare a final report assembling and evaluating all data relating to incineration operations so as to determine compliance with those permit conditions concerning at-sea operations.

1.3 SUMMARY

Incineration of the herbicide took place in a U.S. EPA-designated burn zone approximately 120 miles west of Johnston Atoll, as defined by the following coordinates: 15°45' to 17°45' N latitude and 171°30' to 173°30' W longitude. The relationship of the burn zone to Johnston Atoll and the Hawaiian Islands is shown in Figure 1.

A total of 10,400 metric tons (8780 m^3, 2.31 million gallons) of waste was burned, requiring 714 hours. The average incineration rate was 14.5 metric tons per hour or 7.3 metric tons per hour per incinerator. For all three burns, the average flame temperature was 1500°C as determined by daily optical pyrometer measurements. The average incinerator wall temperature (controller thermocouple) was 1273°C for all three burns. For the three burns, the average combustion effluent flow rate per incinerator was calculated to be 70,700 cubic meters per hour (dry gas at 20°C). Given these average conditions of combustion air and waste feed rates and temperature, the average calculated incinerator residence time was 1.0 second. The incinerator residence time was the time available for a waste molecule to be converted to combustion products.

Stack sampling operations utilized a USAF-OEHL benzene impinger train and a modified U.S. EPA Method 5 train (Lear-Siegler) which incorporated an organic vapor sorbent trap. The USAF-OEHL train was the primary train for acquiring samples for TCDD analysis, whereas the Lear-Siegler train was used to acquire samples to be analyzed for organic species potentially present in the combustion


145°
150°
155°
160°
165°
170°
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180°
175°
170°
165°
160°
155°
25°
20°
15°
10°
5°
0°
5°
10°
15°
MIDWAY IS
FRENCH FRIGATE SHOALS
OAHU
HAWAII
WAKE IS
BURN ZONE
JOHNSTON ATOLL
MARIANAS ISLANDS
SAIPAN
TINIAN
ROTA
GUAM
ENIWETOK IS
KWAJALEIN IS
CAROLINE ISLANDS
FANNING IS
CHRISTMAS IS
SOLOMON ISLANDS
HOWLAND IS
BAKER IS
SAMOA
FIJI ISLANDS

Figure 1. Geographical relationship of burn zone to Johnston Atoll and the Hawaiian Islands.

effluent. The Lear-Siegler train also served as a backup to the USAF-OEHL train. These stack samples were subsequently analyzed to determine how effectively the incineration process destroyed constituents of the waste. Stack samples were acquired by a remotely activated, water-cooled, stainless steel probe capable of traversing the starboard stack diameter of 3.4 meters.

During stack sampling operations, incineration effluent products were simultaneously monitored for total hydrocarbons, carbon monoxide, carbon dioxide, and oxygen. Concentrations of these species were measured in real time to monitor the overall combustion efficiency of the incinerator. Instrumentation for these measurements was housed in a modified shipping container lashed to the ship's deck.

Data from the on-line analyzers and the results of the analyses of the stack samples were used to calculate incineration efficiencies. Combustion efficiencies were calculated from the on-line monitoring data. Four different waste destruction efficiencies were calculated, one from the hydrocarbon analyzer data and three from laboratory analyses. These incineration efficiency terms are defined in Table 1. Average values for the incineration efficiencies are given in Table 2.

Results of the analyses by TRW, WSU, and BCL and of the reduction of the on-line monitoring data indicate that the performance of the Vulcanus' incinerators was consistently greater than 99.9% in terms of combustion and destruction efficiencies for 2,4-D and 2,4,5-T and total organic material. Analyses of first and third burn samples for TCDD led to destruction efficiencies greater than 99.9%. Analyses of second burn samples for TCDD led to destruction efficiencies of >99.89% and >99.87%. The fact that these destruction efficiencies were apparently marginally lower than the required 99.9% was because of problems during the TCDD analyses (Section 4.2.5). Chemical interferences during the TCDD analyses led to higher than usual detection limits. Although TCDD was detected in only part of one of the second burn samples, the detection limits are such that these two destruction efficiencies were calculated to be >99.89% and >99.87% rather than 99.9%. It is considered, therefore, that the chemical interferences

TABLE 1. DEFINITION OF INCINERATION EFFICIENCY TERMS

Efficiency Term		Method of Calculation
Overall combustion efficiency	DE_{CE}	$= 100 \times \frac{[\%\ CO_2] - [\%\ CO]}{[\%\ CO_2]}$
Total hydrocarbon (THC) destruction efficiency	DE_{THC}	$= 100 \times \frac{[\text{THC fed}] - [\text{THC found}]}{[\text{THC fed}]}$
Herbicide Orange (HO) destruction efficiency	DE_{HO}	$= 100 \times \frac{[\text{HO fed}] - [\text{HO found}]}{[\text{HO fed}]}$
TCDD destruction efficiency	DE_{TCDD}	$= 100 \times \frac{[\text{TCDD fed}] - [\text{TCDD found}]}{[\text{TCDD fed}]}$
Chlorinated hydrocarbon (CHC) destruction efficiency	DE_{CHC}	$= 100 \times \frac{[\text{CHC fed}] - [\text{CHC found}]}{[\text{CHC fed}]}$

TABLE 2. SUMMARY OF CALCULATED INCINERATION EFFICIENCIES

	First Burn	Second Burn	Third Burn	Combined 3 Burns
DE_{CE}	99.992	99.989	99.983	99.990
DE_{THC}	99.982	99.992	-[(a)]	99.985
DE_{HO}	>99.999	>99.999	>99.999	>99.999
DE_{TCDD}	>99.99	>99.88	>99.96	>99.93
DE_{CHC}	>99.999	>99.999	>99.999	>99.999

(a) HC Analyzer was inoperative during third burn

and not inadequate incinerator performance caused the marginal destruction efficiencies. The extremely high destruction efficiencies for 2,4-D and 2,4,5-T during the second burn (Section 6) support this contention.

Mostly glass components were incorporated in the sampling trains which stood up well to the corrosive (HCl) combustion effluent. The on-line analyzer system functioned adequately and maintained adequate sensitivity for measuring combustion gases. Some damage to the CO and hydrocarbon analyzers occurred from the corrosive gases passing through them, necessitating more frequent maintenance and calibration. The damage was caused by an engineering oversight which left a cold spot in the system. Condensation thus occurred, and it was the condensate that damaged the instruments. No effects from the unusual shock vibration or saltwater environment were noted.

Incinerator controls and instrumentation were adequate. Redundant incinerator wall thermocouples would be desirable from an operational standpoint because loss of wall thermocouples would shut off incineration and because they cannot be replaced while the incinerators are hot.

The personnel protection procedures described in Section 5 worked satisfactorily. A boundary-isolation method of excluding Herbicide Orange from living areas of the ship was used effectively. There were no major exposures of personnel to Herbicide Orange. Minor exposures occurred during the first burn when the incinerator exhaust plume impinged on the ship. Brief plume impingements (5 to 60 seconds) resulted from burner flameouts caused by a layer of material (later identified as water with traces of arsenic and sodium salts of 2,4-D and 2,4,5-T) floating on top of the waste reaching the burners. Flameouts were avoided subsequently by switching two of the three burners in each incinerator to other tanks when nearing depletion of the waste tank being pumped.

A significant result was derived from on-line monitoring data taken during a traverse across the starboard stack. It was found that wall effects on the combustion effluent gas composition from Herbicide Orange incineration were nonexistent at distances greater than 10 cm from the inside incinerator wall surface. Therefore, incinerator combustion efficiency could be determined using a fixed position probe.

The at-sea incineration of Herbicide Orange was successfully completed. The Permittees complied with all permit conditions related to at-sea operations in the designated burn zone and listed in Section 1.2.

2. DESCRIPTION OF THE M/T VULCANUS

2.1 GENERAL LAYOUT OF VESSEL

The M/T Vulcanus, originally a cargo ship, was converted in 1972 to a chemical tanker fitted with two large incinerators located at the stern. The vessel meets all applicable requirements of the Intergovernmental Maritime Consultative Organization (IMCO) concerning transport of dangerous cargo by tanker. Figure 2 is a picture of the vessel, and Table 3 gives some of the ship's specifications. Both the picture and the table were furnished by Ocean Combustion Services, B.V., Rotterdam, The Netherlands, who manage the vessel.

Because of her size — an overall length of 102 meters, a beam of 14.4 meters, and a maximum draft of 7.4 meters — the Vulcanus is able to

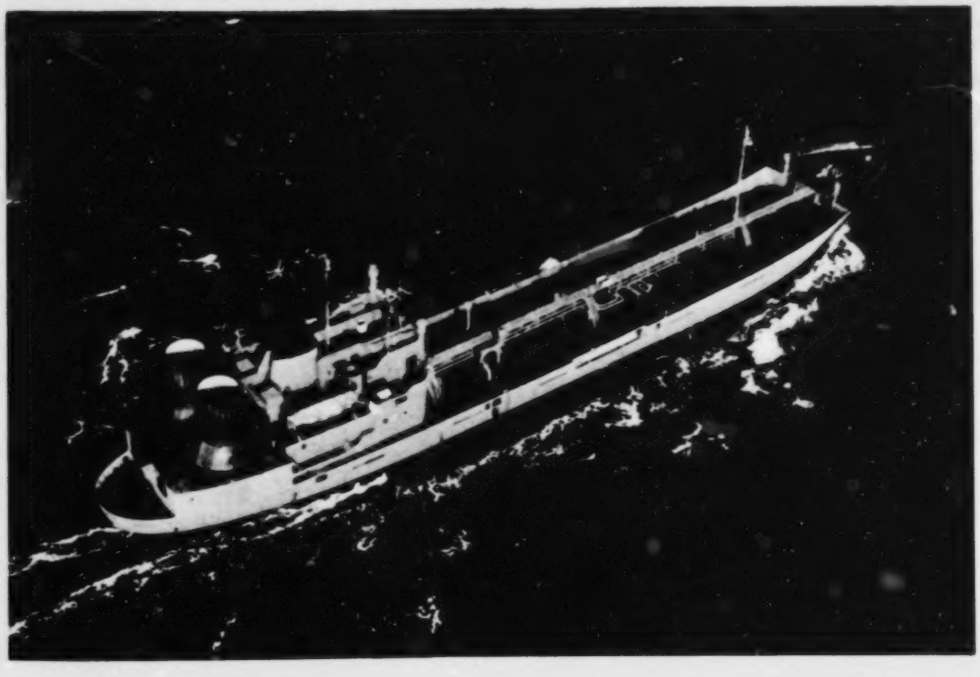

Figure 2. M/T Vulcanus — incineration vessel.

TABLE 3. SPECIFICATIONS OF THE M/T VULCANUS

Length overall	101.95 meters
Breadth	14.40 meters
Draft, maximum	7.40 meters
Deadweight (DWT)	4,768 metric tons
Speed	10-13 knots
Tank capacity	3,503 cubic meters (cu m)
Number of tanks	15, ranging in size from 115 cu m to 574 cu m
Tank coating	No coating in tanks, pipes, pumps, etc. All equipment consists of low carbon steel
Loading equipment	Not available, but can be placed on board, if required
Hose connection	10.2, 15.2, and 20.3 centimeters (4,6, 8 inches)in diameter
Safety equipment	Specially designed for this task and in accordance with latest regulations of IMCO, Scheepvaart-Inspectie (The Hague)
Waste to be processed	Must be liquid and pumpable. May contain solid substances in pieces up to 5 centimeters in size. Must not attack mild steel
Incinerators	2
Per incinerator:	
Overall height	10.45 m
Combustion chamber	
OD	5.5 m
ID	4.8 m
Stack (top)	
OD	3.8 m
ID	3.4 m
Waste feed (max)	12.5 metric tons/hour
Combustion air (max)	90,000 m^3/hour
Burners (Vortex type)	3
Volume	120 m^3
Residence time	1.0 sec at 1500 °C (calculated)

operate worldwide. Two diesel engines drive a single propeller to give cruising speeds of 10 to 13 knots. Her crew numbers 18; twelve to operate the vessel and six to operate the incinerators.

2.2 TANKS AND PUMPS

The Vulcanus is a double-hull, double-bottom vessel. Waste is carried in 15 cargo tanks which range in size from 115 to 574 cubic meters (m^3) with an overall capacity of 3503 m^3. Figure 3 is a schematic of the cargo tank layout. Tanks are filled through a manifold on deck using a dockside loading pump. During normal operation the waste tanks can be discharged only through the incinerator feed system. There is, however, provision for discharging the cargo into the ocean if an emergency arises. Piping system construction makes it possible for any tank to be connected to either incinerator and for cargo to be transferred from one tank to another.

The space between the two hulls is used for ballast. Ballast tanks may be filled with seawater and emptied independently as required to trim and balance the ship. Fuel oil is carried in tanks under and in the engine room. The engine room is separated from the cargo tanks by double bulkheads. The pump room and generator room are situated between the engine room and the waste tanks.

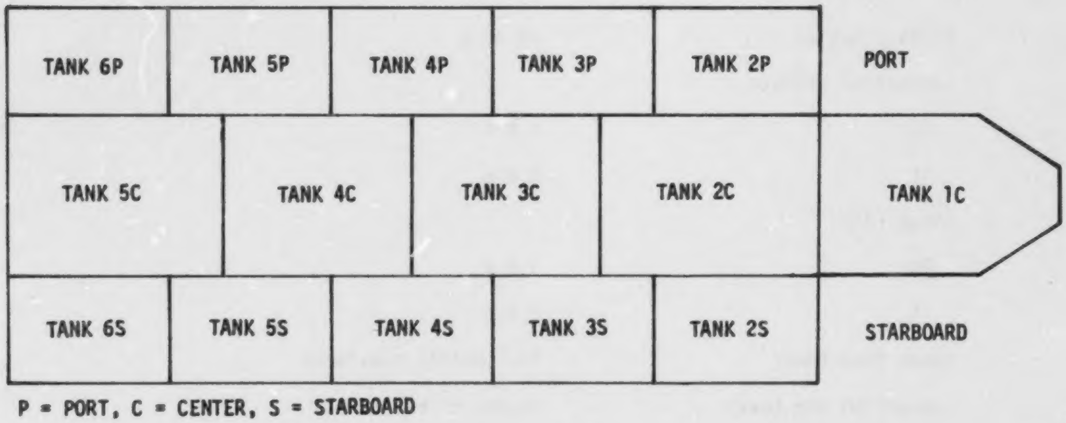
TANK 6P
TANK 5P
TANK 4P
TANK 3P
TANK 2P
PORT
TANK 5C
TANK 4C
TANK 3C
TANK 2C
TANK 1C
TANK 6S
TANK 5S
TANK 4S
TANK 3S
TANK 2S
STARBOARD
P = PORT, C = CENTER, S = STARBOARD

Figure 3. Cargo tank layout schematic.

2.3 INCINERATOR SYSTEM

Waste is burned in two identical refractory-lined furnaces located at the stern. Each incinerator consists of two main sections, a combustion chamber and a stack, through which the combusting gases pass sequentially (Figure 4). This dual chamber configuration, which is characteristic of most high intensity combustion systems, uses the first chamber for internal mixing and the second for adequate residence time. Table 3 gives characteristics of the incinerators.

Combustion air is supplied by large fixed speed blowers with a rated maximum capacity of 90,000 cubic meters per hour for each incinerator. Adjustable vanes are incorporated in the combustion air supply system. When they are deflected, system pressure drop is increased, and the flow rate is reduced. Although no instrumentation is installed to monitor air flow rate, normal

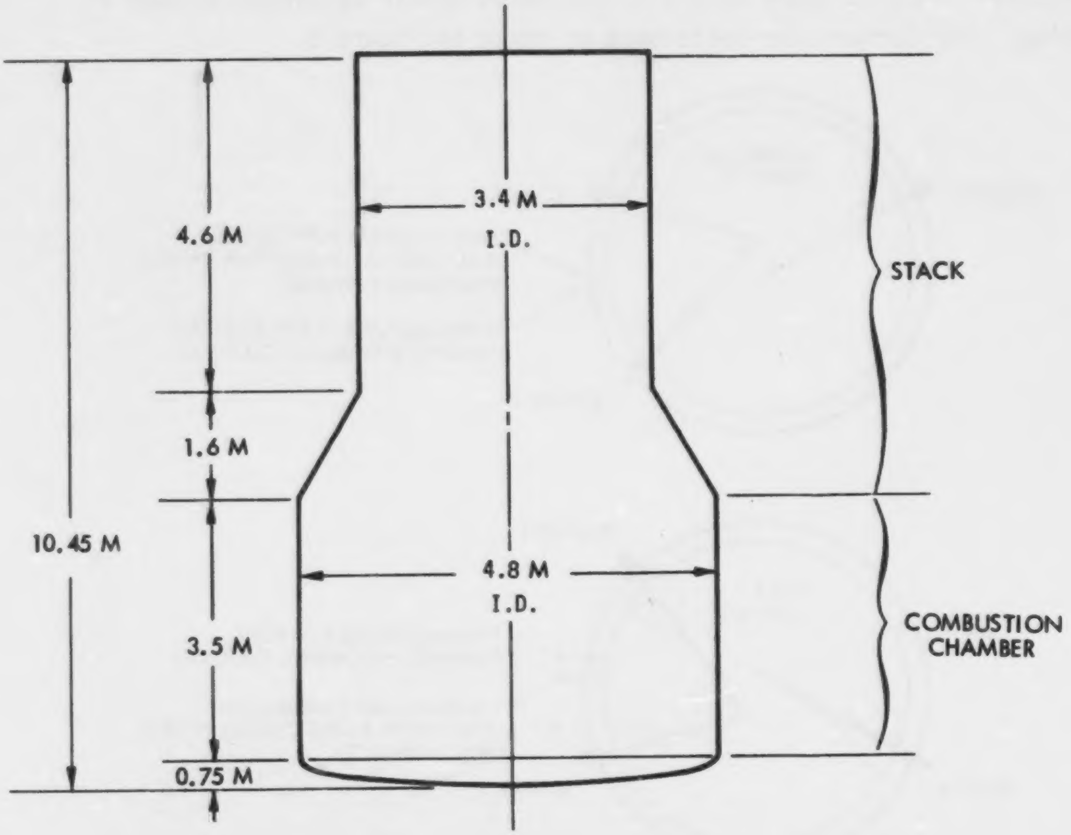

Figure 4. Incinerator configuration.

operation is stated by the ship's chief engineer to be between 75,000 and 80,000 cubic meters per hour at ambient conditions.

Liquid wastes are fed to the combustion system by means of electrically driven pumps. Upstream of each burner supply pump is a device (Gorator) for reducing the solids in the waste to a pumpable slurry. The Gorator also acts as a mixing pump by recirculating the waste through the waste tank. Power for the blowers, pumps and other parts of the incinerator system is supplied by two diesel-generators with a total capacity of 750 kW at 440 volts and 60 Hertz.

Three burners of the vortex type are located at the same level on the periphery of each furnace near its base. The burners are of a rotating cup, concentric design and deliver waste or fuel oil through a central tube to an atomization nozzle, where it meets high velocity air delivered through an annulus. The burners are positioned as shown in Figure 5.

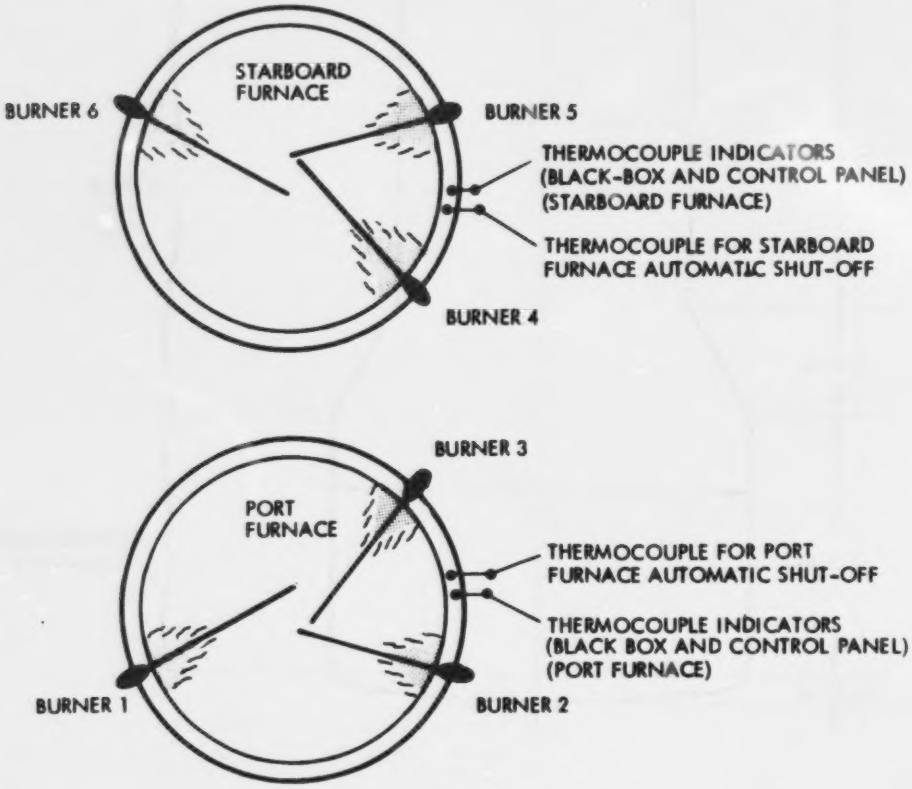
STARBOARD FURNACE
BURNER 6
BURNER 5
THERMOCOUPLE INDICATORS (BLACK-BOX AND CONTROL PANEL) (STARBOARD FURNACE)
THERMOCOUPLE FOR STARBOARD FURNACE AUTOMATIC SHUT-OFF
BURNER 4
BURNER 3
PORT FURNACE
THERMOCOUPLE FOR PORT FURNACE AUTOMATIC SHUT-OFF
THERMOCOUPLE INDICATORS (BLACK BOX AND CONTROL PANEL) (PORT FURNACE)
BURNER 1
BURNER 2

Figure 5. Incineration system — burner and thermocouple locations.

Three-way valves are utilized on each burner to provide either waste feed, fuel oil feed, or a shutoff condition. Waste and fuel oil cannot be valved into a burner simultaneously; however, alternate burners could be operated with fuel and waste to achieve higher or lower combustion temperatures if necessary, depending on the relative heat contents of the fuel oil and waste.

Periodically the burners require cleaning. They are normally cleaned one at a time with the remaining two firing waste. Cleaning is easily accomplished because the burners are readily accessible. Each burner has a vertical pivot so that it can be swung out of the furnace. The opening left by this operation is temporarily closed by a cover. The burners are cleaned by a metal tool which is pushed through the burner.

2.4 RECORDING AND CONTROL EQUIPMENT

2.4.1 Waste Measurements

A new measuring system was installed into each tank for the Herbicide Orange burns. It was a sealed system to prevent waste vapors from escaping. However, this system proved unsatisfactory because it measured only the top one-third of each tank and because the tanks had to be vented to atmosphere in order to pump waste out. Sounding the depth of waste in each tank with a tape was another method of determining burn rate. Both of these methods were only useful in port or in calm seas (i.e., minimum ship roll). During the actual burns, the total time was recorded for emptying each tank and a time averaged waste feed rate was determined.

2.4.2 Wall Temperature Measurements

Temperatures during operation of the incinerators were measured by two platinum-platinum/10% rhodium thermocouples in each incinerator. Each pair is located in a well opposite one of the burners (Figure 5). One thermocouple is located approximately 1.3 cm from the inside surface of the refractory lining. This thermocouple provides temperature information to the automatic waste shutoff system and is called the controller thermocouple. A second thermocouple, approximately 4 cm from the inner surface of the firebrick, is referred to as the "indicator" because it provides temperature information to a panel located in the incinerator control room and to a panel ("black box") located on the bridge.

The thermocouples used to activate the automatic waste shutoff system and the recording equipment have been quite reliable and durable according to personnel of the M/T Vulcanus. There were no failures during the operations covered in this report.

2.4.3 Emergency Automatic Waste Shutoff

A Plastomatic 2000 system (supplied by Withoff-Phillips, Bremen, West Germany) was used for the emergency automatic waste shutoff. This system uses a thermocouple controlled, spring loaded, solenoid actuated valve which shuts off waste to the burners when the temperature of the furnace drops below a preset selected temperature. During these tests the U.S. EPA required the Plastomatic controller to be set such that waste flow would be shut off if the flame temperature dropped below 1250°C.

If the temperature in a furnace should drop below the preselected minimum, the Plastomatic 2000 solenoid is deactivated, allowing a spring loaded valve to close, shutting off the flow of waste to the three burners of that furnace. The valve which is closed shuts the waste line in both directions and also stops the waste pumps by cutting power to them. A power failure or thermocouple burnout in the Plastomatic 2000 system would also shut off the flow of waste to the burners involved.

If the system should shut off the waste flow, the pump which has been stopped and the valves which have been closed may be restarted after the cause has been identified and corrected and after the Plastomatic has been reset. It should be noted that operating procedures require restart and reestablishment of the required flame temperature using fuel oil before waste can be burned again.

The controller thermocouple was also utilized to indicate real-time temperature measurements. This was accomplished by adjusting the controller dial from the shutoff temperature setting to increasingly higher temperature settings. When the adjusted setting was coincident with the actual temperature sensed by this thermocouple, the feed valve relay clicked. Observation of the pointer location with respect to the temperature scale on the dial provided a temperature reading. The waste shutoff system was not immediately activated because a time delay was incorporated in the electrical circuit. The pointer was then reset to the required automatic shutoff temperature before the system activated. The ability to record temperatures in this manner was useful in the event that the indicator wall temperature thermocouple should fail during operation.

2.4.4 Special Equipment

Certain equipment has been installed on the Vulcanus because of its particular type of operation. These items of equipment are:

- Loran and Decca Navigational Systems: This equipment is needed in American (Loran) and European (Decca) waters in order to locate the ship precisely at all times. Celestial navigation was used to locate and keep the Vulcanus in the designated burn zone.
- Anemometer: This equipment measures the velocity and force of the wind. It is, therefore, useful in selecting an attitude of the ship during various wind conditions such that the plume may be directed away from the ship and its personnel.
- Radio Communication: The Vulcanus is equipped with SSB (single side band) and DSB (double side band) radio for voice and continuous wave communication; MF (medium frequency) and SF (short wave) telegraphy; Marifoon (VHF) (all channels) for close-in voice communication; and Semafoon (a private telephonic communication system). For this program, a Hagenuck Synthesized Transceiver was installed to permit voice communication over all marine frequencies. A radio was also located on the bridge so that the watch officer could hear marine broadcasts at all times.
- Optical Pyrometer: A portable optical pyrometer was utilized during the test program to measure incinerator flame temperatures. These measurements were taken daily using a Leeds and Northrup optical pyrometer operating in the 6500 Å range.
- Black Box: On the bridge was a panel in a sealable enclosure referred to as the "black box" which displayed information necessary to assure that wastes were being burned at proper temperatures and, in Europe where the Decca Navigator can receive suitable land based signals, at the proper location. The panel displays included the following information: indicator thermocouple readings for each incinerator; day, month, and time; status (on/off) of the waste pumps; and the vessel's position by the Decca Navigator. An 8 mm movie camera within the black box photographed the panel every 15 minutes during incinerator operations. Films from the incineration of Herbicide Orange were retained by the U.S. EPA.

3. TEST OPERATIONS

3.1 SAMPLING AND MONITORING EQUIPMENT AND PROCEDURES

The combustion product effluent stream from the incineration of Herbicide Orange onboard the M/T Vulcanus was sampled utilizing three probes. Two ceramic probes (one in each stack) were installed to divert the gases to an on-line monitoring system comprised of CO, CO_2, O_2, and hydrocarbon analyzers. For a more comprehensive characterization of the combustion effluent chemical species, including specific herbicide constituents, a water-cooled probe capable of traversing the starboard incinerator diverted a representative portion of the effluent stream to two sampling trains. These sampling trains were: (1) the USAF-OEHL benzene impinger train which was previously tested and proven effective for sampling 2,4-D, 2,4,5-T, and TCDD, and (2) a modified U.S. EPA Method 5 train which incorporated a sorbent trap that has been used extensively for the general trapping of organic compounds in commercial incineration of organochlorines. The USAF train was the primary train for acquiring the samples for TCDD analysis, whereas the sorbent train acted as a backup system for TCDD, as well as the primary train for the determination of organic species potentially present in the effluent.

In addition to stack sampling, a variety of air, liquid, and solid samples were taken. These samples included:

- Plankton and seawater samples - Plankton and seawater tows were made in the burn zone before and after incineration of the first shipload.
- Tedlar® bag stack gas grab samples - Samples of the stack gas obtained from the gas conditioner were taken to supplement the XAD-2® module information. Each sample was 28 liters in volume.
- Burner residues - Samples of burner residue were taken when the burners were cleaned.

- Composite waste feed - Samples of waste being fed to the incinerators were taken for determination of the composition of the waste. These samples were taken at burner No. 4 rather than from the tanks.
- HCl measurements - Air was sampled with a Drager® apparatus during incinerator operations to detect whether the plume was contacting the ship.
- Air samples - Ambient air grab samples were taken at specific locations using a gas syringe and analyzed for 2,4-D and 2,4,5-T by an onboard gas chromatograph.
- Wipe samples - Whatman 41® filter papers were used to wipe selected areas of the ship. They were extracted and analyzed by the onboard GC for 2,4-D and 2,4,5-T.
- Workspace air monitors - MSA personnel monitors fitted with Chromosorb 102® absorption tubes were placed at several positions on the ship to monitor personnel exposure to 2,4-D and 2,4,5-T.

Samples of stack gas, burner residues, and composite feeds were taken for completeness of sampling, and results are given in Section 4. HCl measurements, air samples, wipe samples, and workspace air monitor samples were taken as part of the personnel protection plan and are discussed in Section 5.

3.1.1 On-Line Monitoring System/Portable Laboratory

A standard shipping container was modified as a portable laboratory to house the on-line monitoring instrumentation and to serve as the operations room for the sampling team. Its overall dimensions were 2.4 x 6.1 x 2.4 m. It was constructed of 2.54 cm plywood with an exterior fiberglass coat and was built on a base of approximately 15 cm longitudinal and transverse structural steel channels and beams. A hardwood floor of 5 cm dimensioned lumber was provided, and all corners had cast metal stacking and tie-down provisions for securing the container to the ship's deck.

The container tare weight was 1,800 kg, and maximum gross weight was 20,000 kg. It is estimated that the total weight of the equipment and container was 8,700 kg. It can be forklifted or hoisted by slings, and it is structurally sound for stacking. The portable laboratory was stacked above an identical container, which was used for storage of supplies and spares. The stacking arrangement on the ship met U.S. Coast Guard requirements. Figure 6 gives a view of the equipment arrangement in the portable laboratory.

Power for the portable laboratory and sampling equipment was provided by a motor generator which converted the 440 V, 60 Hz ship's power to 110 V, 60 Hz. This motor generator was installed on the observation deck, above the bridge. A backup motor generator was similarly installed.

3.1.1.1 Fixed Probe Design

The probe used for the on-line gas analyzers was in addition to the sampling equipment previously used on the Vulcanus. The probe was a 122- by 1.27-cm OD high temperature alumina tube with a 1.6 mm wall. This ceramic material was inert and had been shown to operate well in similar environments. It required no cooling and was fixed in place (i.e., it would not traverse). One of these probes was installed in each incinerator stack and extended about 38 cm (15 in.) past the inner wall. Heat traced Teflon® lines connected these probes to a three-way valve. This valve was connected to a manifold in the portable laboratory leading to two parallel gas analysis systems. Figure 7 is a schematic of the probe and heat traced line layout. This design made it possible to monitor either incinerator with either gas analysis system although both incinerators could not be monitored simultaneously.

3.1.1.2 Instrumentation

On-line monitoring of the concentrations of selected gases in both incinerator effluents was accomplished by two complete duplicate systems schematically depicted in Figure 8. These measurements served as indices of the effectiveness of the thermal destruction process. The on-line monitors used one ceramic probe in each stack with heated line delivery systems. This allowed random monitoring of the incinerators regardless of the status of the other trains. The monitors and their calibration ranges are shown in Table 4. The manifold system was designed so that either a complete bank of instruments or one instrument can be operated depending on the operational readiness of any given instrument. Besides availability of duplicate analyzers, spare parts were carried onboard.

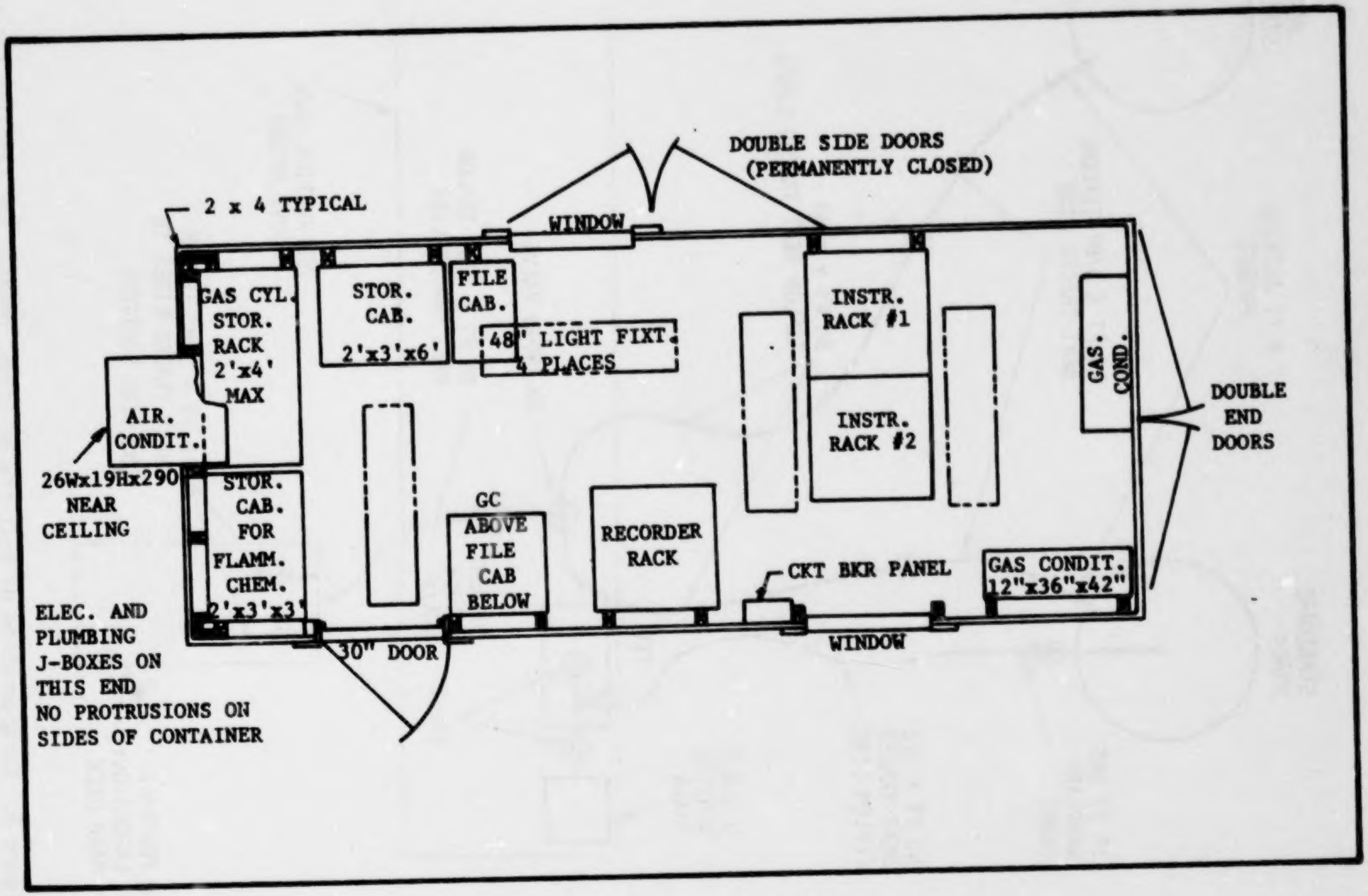
DOUBLE SIDE DOORS
(PERMANENTLY CLOSED)
2 x 4 TYPICAL
WINDOW
GAS CYL. STOR. RACK 2'x4' MAX
STOR. CAB. 2'x3'x6'
FILE CAB.
48" LIGHT FIXT. 4 PLACES
INSTR. RACK #1
INSTR. RACK #2
GAS. COND.
DOUBLE END DOORS
AIR. CONDIT.
26Wx19Hx290 NEAR CEILING
STOR. CAB. FOR FLAMM. CHEM. 2'x3'x3'
GC ABOVE FILE CAB BELOW
RECORDER RACK
CKT BKR PANEL
GAS CONDIT. 12"x36"x42"
ELEC. AND PLUMBING J-BOXES ON THIS END
NO PROTRUSIONS ON SIDES OF CONTAINER
30" DOOR
WINDOW

Figure 6. Layout of portable laboratory.

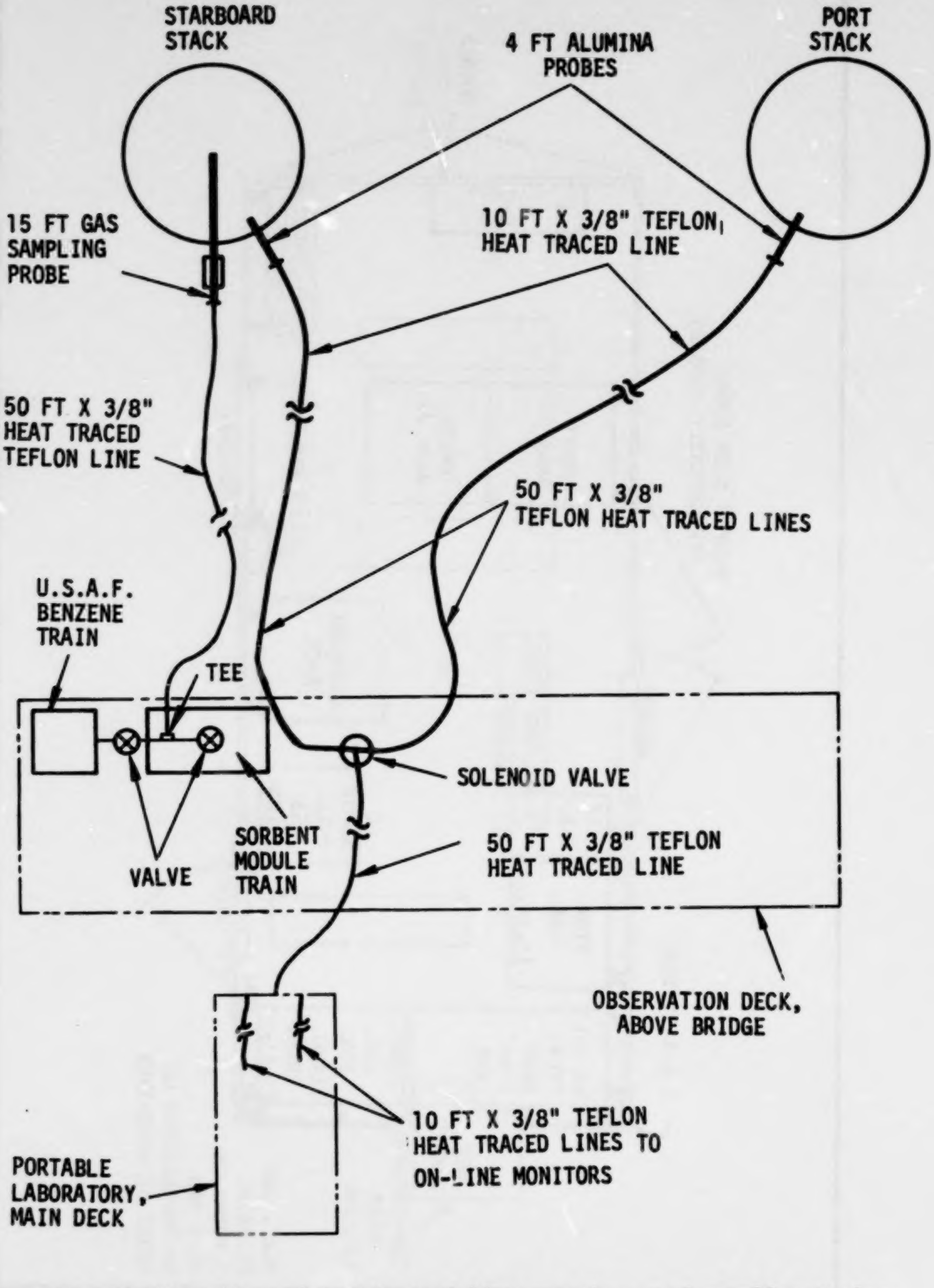
STARBOARD STACK
4 FT ALUMINA PROBES
PORT STACK
15 FT GAS SAMPLING PROBE
10 FT X 3/8" TEFLON HEAT TRACED LINE
50 FT X 3/8" HEAT TRACED TEFLON LINE
50 FT X 3/8" TEFLON HEAT TRACED LINES
U.S.A.F. BENZENE TRAIN
TEE
SOLENOID VALVE
VALVE
SORBENT MODULE TRAIN
50 FT X 3/8" TEFLON HEAT TRACED LINE
OBSERVATION DECK, ABOVE BRIDGE
10 FT X 3/8" TEFLON HEAT TRACED LINES TO ON-LINE MONITORS
PORTABLE LABORATORY, MAIN DECK

Figure 7. Configuration of heat traced lines, probes, and sampling trains.

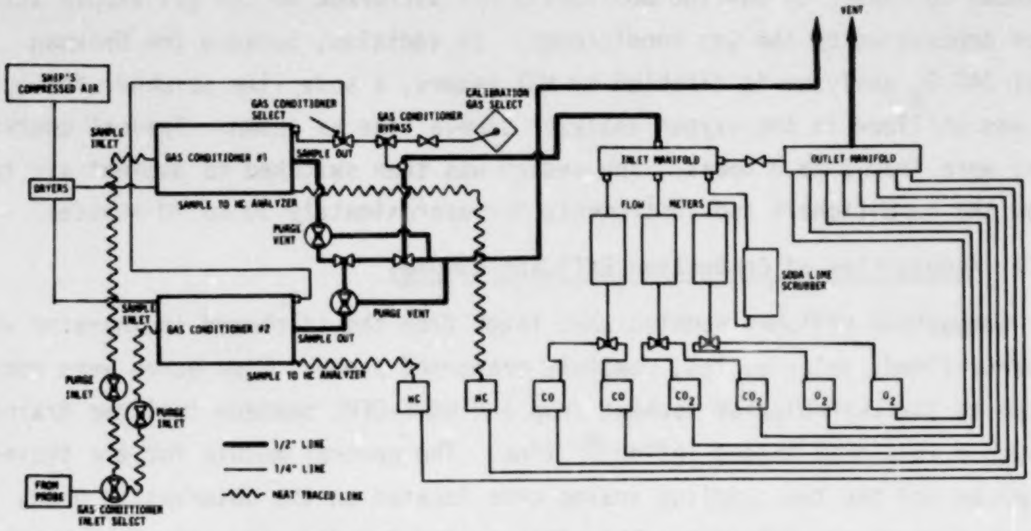
VENT
SHIP'S COMPRESSED AIR
GAS CONDITIONER SELECT
GAS CONDITIONER BYPASS
CALIBRATION GAS SELECT
SAMPLE INLET
GAS CONDITIONER #1
SAMPLE OUT
INLET MANIFOLD
OUTLET MANIFOLD
DRYERS
SAMPLE TO HC ANALYZER
FLOW METERS
PURGE VENT
SODA LIME SCRUBBER
SAMPLE INLET
GAS CONDITIONER #2
PURGE VENT
SAMPLE OUT
SAMPLE TO HC ANALYZER
PURGE INLET
PURGE INLET
HC
HC
CO
CO
CO2
CO2
O2
O2
1/2" LINE
1/4" LINE
HEAT TRACED LINE
FROM PROBE
GAS CONDITIONER INLET SELECT

Figure 8. Schematic of on-line monitoring system.

TABLE 4. ON-LINE MONITORS

Species Analyzed	Mfg and Model	Analyzer Type	Instrument Range
Hydrocarbons (HC)	Beckman 402	FID heated	0.05 ppm to 10% in 8 ranges
Carbon Monoxide (CO)	Beckman 865	NDIR	0-200 ppm, 0-2000 ppm, 0 - 2%
Carbon Dioxide (CO_2)	Beckman 864	NDIR	0 - 4%, 0 - 8% 0 - 15%
Oxygen (O_2)	Beckman 742	Electro-chemical	0 - 5%, 0 - 10% 0 - 25%
Oxygen (O_2)	Taylor 0247A	Paramagnetic	0 - 5%, 0 - 10% 0 - 25%

As shown in Figure 8, on-line monitoring was performed on the gas sample stream after processing by the gas conditioner. In addition, because the Beckman Model 747 O_2 analyzer is disabled by HCl vapors, a soda lime scrubber for acid gas was utilized in the oxygen analyzer sample line as shown. Typical operating times were from 1 to 3 hours. The system was then switched to ambient air to purge the conditioners and instruments for approximately 30 to 60 minutes.

3.1.2 Acquisition of Combustion Effluent Samples

Combustion effluent samples were taken from the starboard incinerator using a quartz-lined, water-cooled, remotely traversed probe. Flue gases were conducted to the Lear-Siegler sorbent trap and USAF-OEHL benzene impinger trains through a 15 m heat traced Teflon® line. The control module for the traversing probe and the two sampling trains were located on the observation deck, the topmost deck of the Vulcanus. This deck is located directly above the bridge and forward of the funnel (Figure 2).

3.1.2.1 Traversing Probe

The common probe for the two sampling trains was a stainless steel jacketed, water-cooled probe with a quartz liner as shown schematically in Figure 9. The liner provided an inert surface for the sample gas, and the cooled stainless steel jacket shielded this gas from extreme combustion temperatures to quench any further reactions of the sample constituents. Water cooling also protected the metal probe from warping or otherwise being degraded in the extreme temperatures. Further cooling of the gas was modulated by aspirating an air/water mixture into the space between the steel jacket and quartz liner. The probe was approximately 4.6 m in length.

Figure 10 shows the water-cooled traversing probe mount installation for the Vulcanus. Design features for this probe mount are given below:

1) The tip of each probe was remotely positionable for the amount of insertion. No adjustment was required for azimuth and elevation.

2) Insertion positioning accuracy was within ±10 cm by command from a remote location.

3) The probe mount was attached to the incinerator flange as shown in Figure 10. The outboard end of the mount assembly was supported by an A-frame secured to the deck.

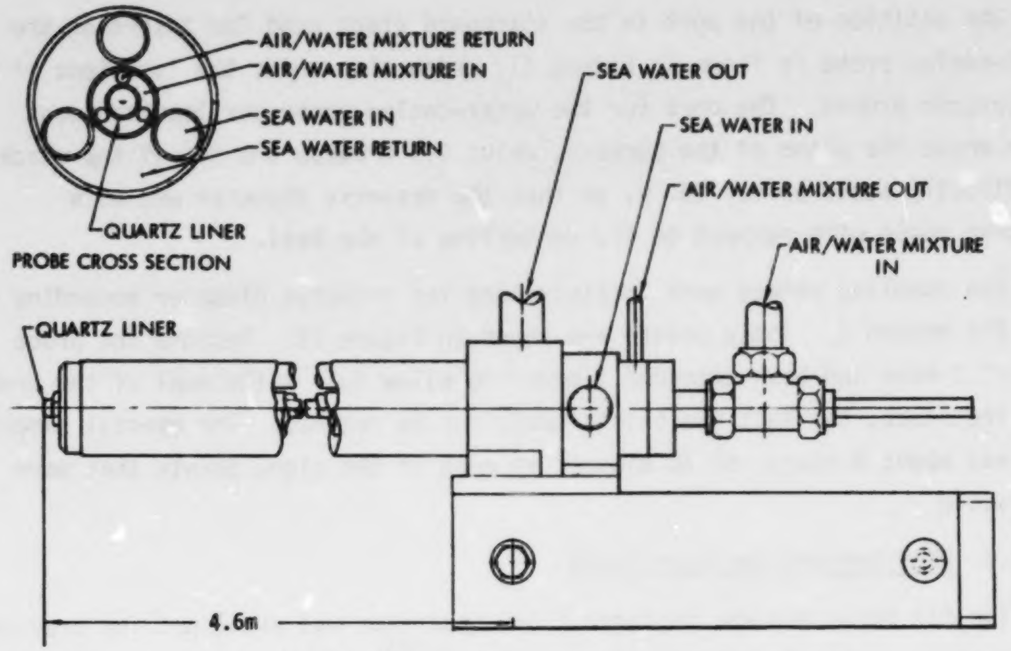
AIR/WATER MIXTURE RETURN
AIR/WATER MIXTURE IN
SEA WATER IN
SEA WATER RETURN
QUARTZ LINER
PROBE CROSS SECTION
SEA WATER OUT
SEA WATER IN
AIR/WATER MIXTURE OUT
AIR/WATER MIXTURE IN
QUARTZ LINER
4.6m

Figure 9. Probe design.

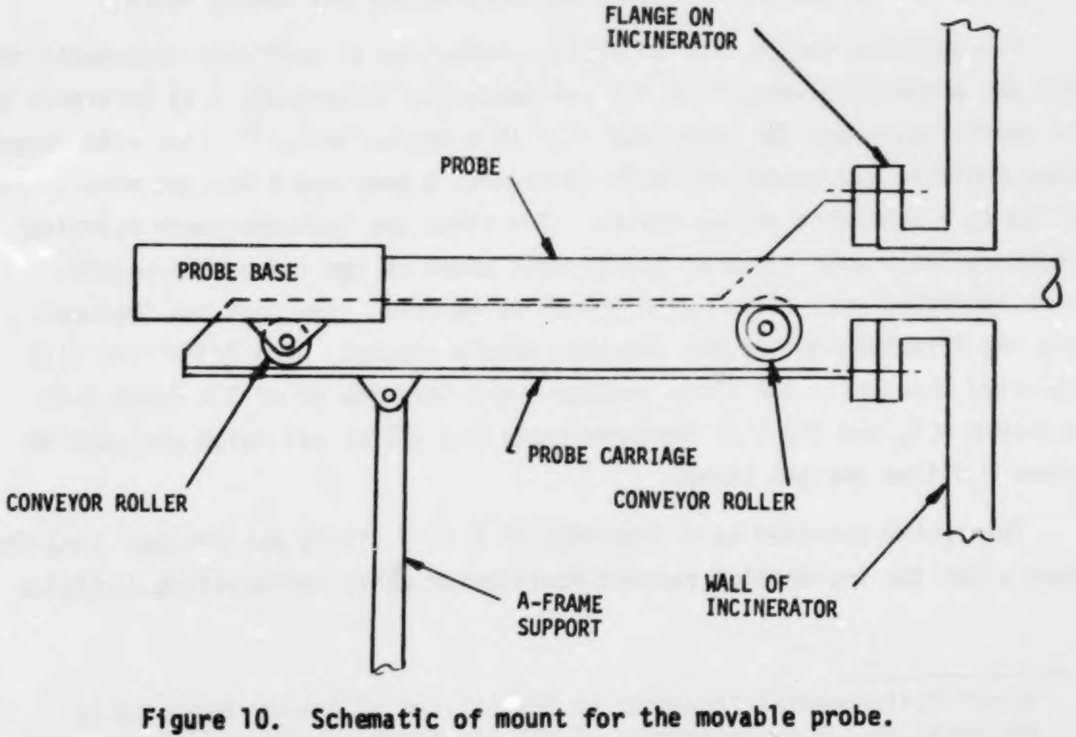
FLANGE ON INCINERATOR
PROBE
PROBE BASE
CONVEYOR ROLLER
PROBE CARRIAGE
CONVEYOR ROLLER
WALL OF INCINERATOR
A-FRAME SUPPORT

Figure 10. Schematic of mount for the movable probe.

The position of the port in the starboard stack used for inserting the water-cooled probe is shown in Figure 11, which also shows the locations of the two ceramic probes. The port for the water-cooled probe was located about 7.6 m above the plane of the burners, about 0.9 m below the top of the stack, and directly above burner No. 6, so that the traverse diameter was at a 6-degree angle with respect to the centerline of the keel.

Ten sampling points were located along the traverse diameter according to U.S. EPA Method 1. These points are shown in Figure 12. Because the probe support I-beam had been extended 1 meter to allow full withdrawal of the probe from the stack, the last two points could not be reached. The overall sampling time was about 4 hours, or 30 minutes at each of the eight points that were accessible.

3.1.2.2 USAF Benzene Impinger Train

The Air Force benzene impinger train apparatus was developed for previous incineration tests of Herbicide Orange in 1973(2). Equipment and sampling techniques were validated in a test program based upon mass balance of known herbicide constituents fed to this sampling train versus the amount found.

The sampling system used to monitor emissions of herbicide components and TCDD was a modified version of the one described in Appendix E of Reference 2. The modification was the insertion of a 15 m heated Teflon® line with temperature monitor, six Greenburg-Smith impingers, a pump and a dry gas meter. Figure 13 is a schematic of the system. The first two impingers were modified Greenburg-Smith with a coarse quartz frit added to the end of the nozzle. These impingers were filled with 350 ml of benzene. The next two impingers, with the Greenburg-Smith type impactor nozzle removed, were 2/3 filled with activated charcoal. The fifth impinger contained 240 ml of 30% (w/v) NaOH to absorb HCl, and the last impinger contained silica gel which was used to remove H_2O from the gas stream.

The system operated at a flow rate of 2 to 3 liters per minute. Sampling began after the incinerator reached equilibrium while incinerating Herbicide

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2. "Final Environmental Statement on Disposition of Orange Herbicide by Incineration," U.S. Department of the Air Force, November 1974.

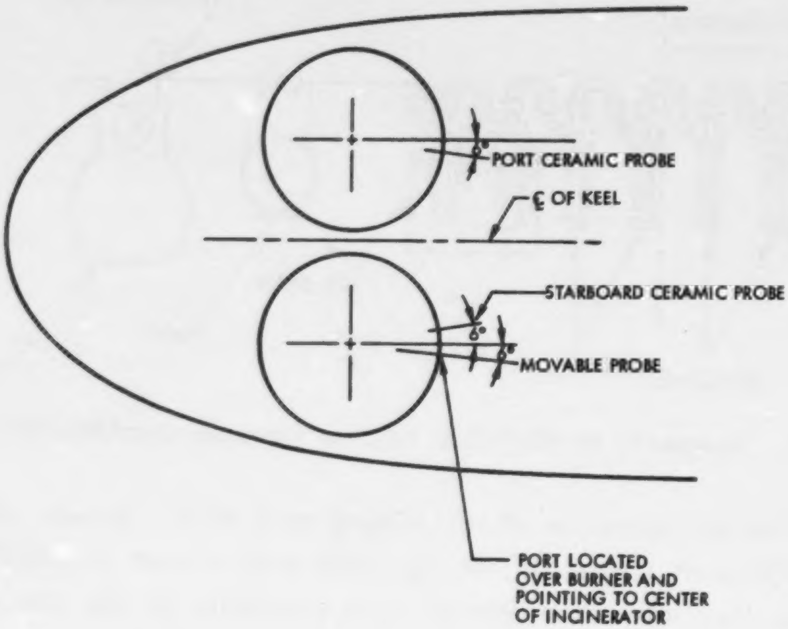
6°
PORT CERAMIC PROBE
℄ OF KEEL
STARBOARD CERAMIC PROBE
6°
6°
MOVABLE PROBE
PORT LOCATED
OVER BURNER AND
POINTING TO CENTER
OF INCINERATOR

Figure 11. Sampling port locations.

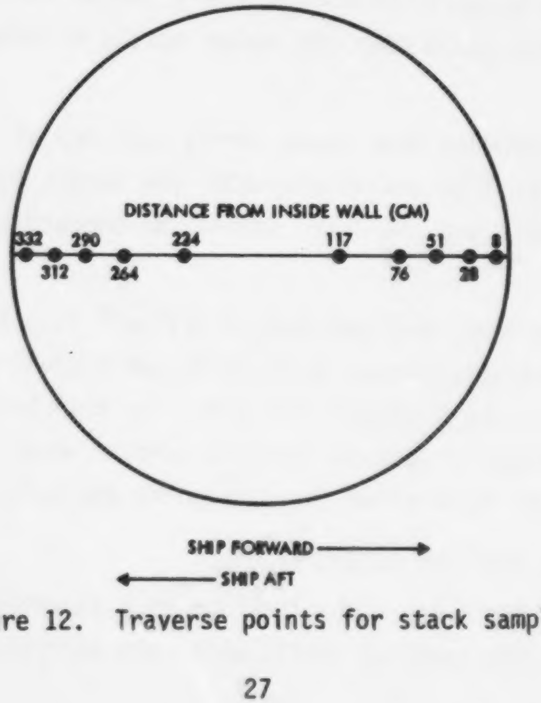
DISTANCE FROM INSIDE WALL (CM)
332
312
290
264
224
117
76
51
28
8
SHIP FORWARD
SHIP AFT

Figure 12. Traverse points for stack sampling.

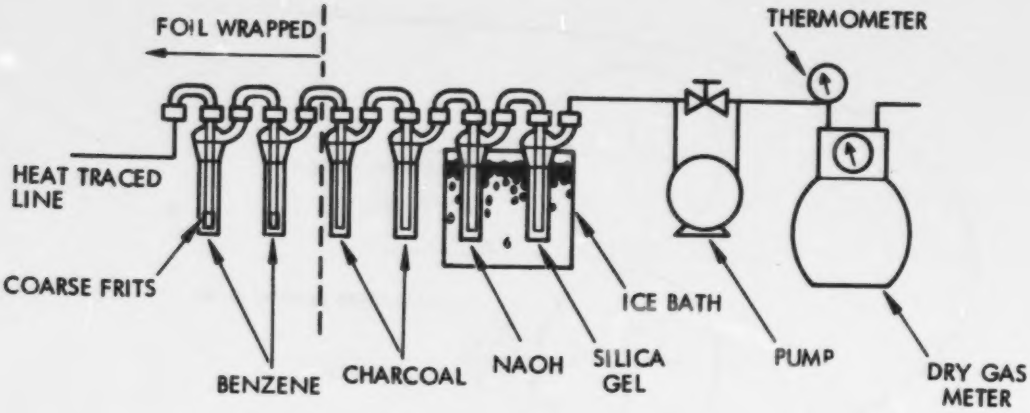

Figure 13. Schematic of USAF-OEHL benzene impinger sampling train.

Orange and during the operation of the sorbent trap train. Because of the sensitivity of TCDD to UV light, benzene impingers were wrapped in aluminum foil. Once assembled, they were not reopened. Upon completion of the 1-hour sampling period, contents of the impingers and connectors were transferred to amber glass containers. Benzene addition, sample removal, and acetone rinsing were accomplished by pouring the solvents through the ball joints using a glass or Teflon® funnel. All rinses were added down the center nozzle to ensure completeness of rinsing.

Three USAF train samples were taken during each day of stack sampling. One sample was taken for TCDD analysis by WSU, one sample for analysis of 2,4-D and 2,4,5-T by BCL, and the third sample for onboard analysis of 2,4-D and 2,4,5-T by TRW.

At the end of the test, the heat traced Teflon® line and probe were rinsed with acetone and transferred to separate amber glass containers. All sample containers were stored aboard ship until the test burn was completed. After the Vulcanus docked at Johnston Island, samples were shipped by the U.S. Air Force to the proper destination for subsequent analysis.

3.1.2.3 Sorbent Trap Sampling System

The sorbent trap train was a modification of a standard Lear-Siegler U.S. EPA Method 5 train. This sampling train, which has approximately a 1 cfm

(28 ℓ/m) sampling rate capability, is shown schematically in Figure 14. Several important features are noteworthy:

- The water-cooled, quartz-lined probe was used to obtain the sample.
- A solid sorbent trap was located in the sample line downstream of (after) the heated line and upstream of the first impinger. This trap was designed to trap the organic constituents. A bed of granular XAD-2® resin was used for the sorbent. The module that houses the sorbent trap was water jacketed. Cold water from the ice bath surrounding the impingers was pumped into the jacket to maintain a gas out temperature of ≤16°C.

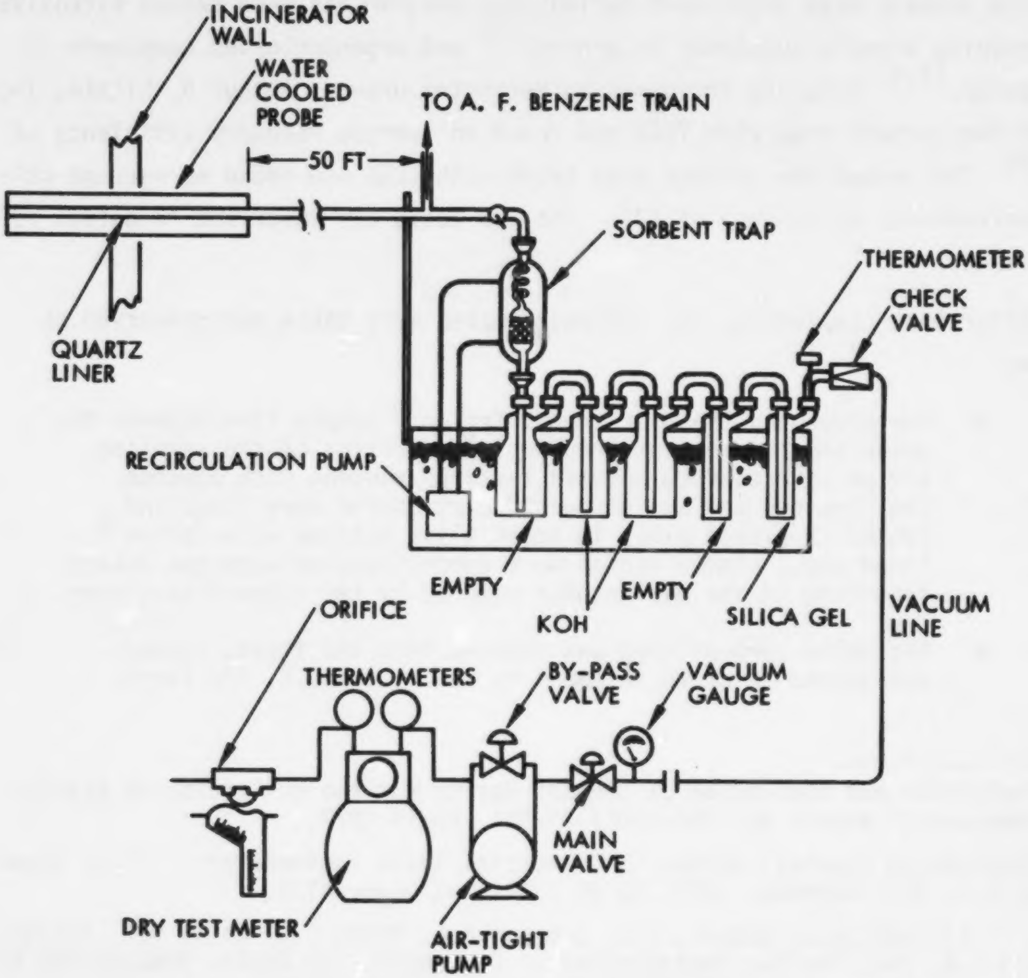
INCINERATOR WALL
WATER COOLED PROBE
TO A. F. BENZENE TRAIN
50 FT
SORBENT TRAP
THERMOMETER
CHECK VALVE
QUARTZ LINER
RECIRCULATION PUMP
EMPTY
KOH
EMPTY
SILICA GEL
VACUUM LINE
ORIFICE
THERMOMETERS
BY-PASS VALVE
VACUUM GAUGE
MAIN VALVE
DRY TEST METER
AIR-TIGHT PUMP

Figure 14. Schematic of Lear-Siegler stack sampling train.

- Additional large capacity (2-liter) impingers were added to the train to permit sampling for 4 hours without having to replace the NaOH acid scrubbing impingers or to remove the excess moisture trapped in the impingers.

- Because the sorbent material has poor trapping efficiency for low molecular weight, high volatility organic species in the C_1 to C_6 range, it was necessary to supplement the organic sorbent trap sample. An integrated, composite grab gas sample was taken utilizing 28-liter Tedlar® gas sample bags. The gas sample was taken at the Beckman gas conditioner (Figure 6) which minimized sample alteration and facilitated the sampling operation.

The sorbent trap train used during this program has been tested extensively for trapping organic compounds in general(3) and organochlorine compounds in particular.(4,5) Prior to incinerating Herbicide Orange, Arthur D. Little, Inc., tested the sorbent trap with TCDD and found an average recovery efficiency of 65%.(3) TRW tested the sorbent trap train with TCDD and found an average collection/recovery efficiency of 62%. The TRW tests are described in detail in Appendix E.

After test completion, the various samples were taken and preserved as follows:

- The probe and the heat traced Teflon® sample line between the probe and the sorbent trap/impinger portion of the sampling trains were cleaned between tests by rinsing with acetone. The rinsings and any dislodged particulate were saved and stored in a cool place in amber glass bottles with Teflon® - lined caps. These rinses were apportioned on Johnston Island according to the gas volumes sampled by the respective trains.

- The solid sorbent trap was removed from the train, capped, and stored prior to shipment to TRW by the U.S. Air Force.

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3. "Selection and Evaluation of Sorbent Resins for the collection of Organic Compounds," Report No. EPA-600/7-77-044, April 1977.

4. "Destroying Chemical Wastes in Commercial Scale Incinerators," Final Report to U.S. EPA, November 1977, to be published under NTIS.

5. J.F. Clausen, H.J. Fisher, R.J. Johnson E.L. Moon, C.C. Shih, R.F. Tobias, and C.A. Zee, "At-Sea Incineration of Organochlorine Wastes Onboard the M/T Vulcanus," Report No. EPA-600/2-77-196, September 1977.

- The total volume of liquid in the impingers was measured to determine moisture corrections for sampled gas volume.

3.2 TEST COMMENTARY AND PROBLEMS

3.2.1 First Burn Commentary and Problems

The Vulcanus arrived at Johnston Island on the morning of 11 July 1977. For the next 3 days the ship was outfitted with the sampling probes, lines and other equipment. Part of the outfitting had been accomplished on land prior to the arrival of the Vulcanus. In particular, the instruments had been checked out and calibrated. When the ship arrived, the storage container was removed from the ship and emptied of the probe, A-frame probe support, gas cylinders, and other equipment. The storage container was then reloaded and the portable laboratory placed on top. Both containers were then lashed to the deck. A servicing platform was built below the probe support, and a walkway was constructed from the ship's central catwalk to the portable laboratory.

On 13 July the Vulcanus left port for the burn site and arrived early on 14 July. Pre-incineration plankton tows were performed, as described in Section 3.3. The incinerators were then heated with fuel oil. Once flame temperatures reached 1280°C, a fuel oil background test was started. Upon completion, burner changeover to Herbicide Orange was started at 1540 hours on 14 July. Incineration of the first shipload was completed at 0225 hours on 24 July. Post-incineration plankton tows were performed. The Vulcanus returned to Johnston Island on 25 July.

The weather was pleasant, the seas reasonably calm, and the wind was steady at 9 to 12 m/sec (18 to 24 knots). The incinerator plume was not visible except when ammonia was injected at the tops of the incinerators. A series of photographs were taken by the U.S. Navy during a flyover mission.

Generally, the sampling went smoothly, especially after the first two runs were completed. By that time, most of the minor problems and procedural difficulties had been eliminated. A persistent problem was the difficulty in attaining effluent sample gas outlet temperatures above 100°C in the traversing probe. Thermocouples and flow rates were checked to eliminate any faulty readings. It was finally determined that because the probe was designed for a 5 cfm gas flow, the low (0.8 to 1 cfm) flow rates exceeded the temperature control design.

Even using a heated gas stream in the air cooling portion of the probe did not appreciably change the sample gas outlet temperature. The result of this problem probably was the collection of a larger fraction of high boiling point materials in the probe than would be collected at the higher (150° to 200°C) operating temperature. This problem was circumvented by more frequent rinsing of the probe. Because the ship was rolling between 10 to 20 degrees from vertical, the probe rinsing was difficult.

The vast majority of problems were minor. These were:

- Leaks: A leak at the thermocouple joint of the Lear-Siegler train was corrected with additional sealant. Transportation had caused a number of fittings in the pneumatic systems of the portable laboratory to loosen. The loose fittings were easily tightened.

- Wireless pickup by onboard instruments. Radio communications were picked up by the test equipment. In particular, the onboard gas chromatograph was completely inoperative during voice or continuous wave transmissions.

- Electrical interference: The solenoid valves on the gas conditioners gave rise to small signals which were picked up by the on-line instrumentation recorders.

- Plugs in heat traced lines: Condensate and particulate material shed by the incinerators caused frequent partial plugs in the heat traced lines. The lines were cleaned without difficulty.

- Corrosion: The combustion effluent was quite corrosive because of its HCl content and corroded stainless steel fittings; however, no failures occurred.

- Instrument damage: The gas conditioners were ineffective in removing condensate from the sample stream. The condensate damaged one of the CO analyzers. Rearrangement of the inlet and outlet manifolds of the on-line instrumentation prevented further damage.

There were several instances during the first burn when one or more burners were briefly extinguished (5 to 60 seconds) by water (determined after the burn to be 99% water, about 1% sodium salts of 2,4-D and 2,4,5-T, and about 80 ppm arsenic) floating on top of the herbicide in certain tanks. When flameouts occurred, pumping from that tank was stopped manually by the Chief Engineer who switched the incinerators to other waste tanks. The remaining material in that tank was retained pending resolution after completing the first burn.

The Plastomatic 2000 control system did not instantaneously shut off the flow of material to the incinerators. There is a built-in electrical circuit time delay in this system of unknown but presumably short duration. In addition, controller thermocouples are imbedded in the incinerator firebrick walls and are not directly exposed to the flame environment. Consequently, a thermal lag exists between a decrease in flame temperature and the corresponding reduction in firebrick temperature sensed by the controller thermocouple. This thermal lag is also of unknown duration. Total time lag (electrical plus thermal) of the system exceeded the brief durations of the flameouts.

During the post-burn debriefing on Johnston Island, procedures were developed to flash (evaporate) the contaminated water and to avoid plume impingements caused by flameouts. Full discussions of the flameouts and procedures are given in Section 5.

3.2.2 Second Burn Commentary and Problems

The M/T Vulcanus sailed from Johnston Island at 0830 hours on 6 August 1977. At 2030 hours on 6 August a star fix indicated the ship was within the burn zone, and at 2144 hours the first burner was changed from diesel oil feed to herbicide feed. The on-line monitor system obtained data throughout the changeover period. The Vulcanus finished the second shipload of herbicide at 2000 hours on 16 August 1977 and docked at Johnston Island at 0800 on 17 August.

Throughout the second burn, weather and sea conditions were much milder than during the first burn. The wind speed was quite stable, averaging 10 m/sec (20 knots). There were no plume impingements. The procedure developed after the first burn to prevent flameouts worked satisfactorily. Sampling and monitoring activities were accomplished as planned.

Inoperative CO and hydrocarbon analyzers had been sent back to the manufacturer for refurbishment after the first burn. The instruments were returned in time for installation before sailing for the second burn. In addition, the U.S. Air Force supplied a third CO analyzer.

Because of the first burn flameouts, residual material was left in several tanks (Section 4.1.2). The residuals were sampled and analyzed after returning to Johnston Island. Most of the residual material was herbicide, but there was a layer of water (on top of the herbicide) which contained about 1% sodium salts of 2,4-D and 2,4,5-T and about 80 ppm of arsenic. This material was consolidated into tank 6P. In addition, tank 6P was then filled with herbicide from Johnston Island. It was planned to flash the water layer through the starboard stack by feeding one burner from tank 6P and the other two burners from tanks 3S and 3P. It was planned to acquire a stack sample and on-line data during the flashing. However, the flashing period lasted only a few minutes. Therefore, no stack sample was acquired. Flame temperatures were observed with the optical pyrometer every 5 minutes during this period, and the lowest temperature observed was 1408°C.

There were no major problems encountered during the second burn. The on-line instrumentation was the source of continuous minor problems, especially the CO and hydrocarbon analyzers and the gas conditioners. Alteration of the inlet and outlet manifolds to the on-line instruments prevented the accumulation of condensate which had damaged instruments during the first burn, but the CO analyzers tended to be noisier than during the first burn and required more frequent adjustment and balancing. On 11 August, no on-line data were acquired because all three CO analyzers were inoperative. The refurbished hydrocarbon analyzer was inoperative because the proportional temperature controllers operated improperly (both controllers were on continuously). Parts from the refurbished HC analyzer were used to keep the other HC analyzer operating. About halfway through burn two, one gas conditioner began leaking stack gas into the portable laboratory. Switching gas conditioners alleviated the problem. Because of these problems, on-line monitoring was limited to 1 hour per day.

The incinerators shed particulates from the firebrick linings which caused frequent plugging of the heat-traced lines.

A minor problem was the loss of voice communication with Johnston Island on 11 August. The M/T Vulcanus could not transmit but could receive voice communications. Thereafter, communication from the M/T Vulcanus was by continuous wave. Communications were slower and more cumbersome, but no problems were caused by the loss of voice communication.

3.2.3 Third Burn Commentary and Problems

The M/T Vulcanus sailed from Johnston Island for the third burn at 1905 hours on 23 August 1977 and entered the burn zone at 0600 hours on

24 August. The changeover from diesel fuel to herbicide was completed by 0800 hours. On-line data were acquired during the changeover in the starboard stack. At 1608 hours on 2 September, the last of the contaminated herbicide was burned, and all burners were switched to the uncontaminated (TCDD-free, detection limit of <0.02 ppm) herbicide that had been used to rinse the ship's tanks in accordance with the U.S. EPA approved tank rinsing procedure. At 1150 hours on 3 September, the last of the TCDD-free herbicide tank rinsate had been burned. The Vulcanus then left the burn zone and docked at Johnston Island at 1330 hours on 4 September 1977.

During the first week of the third burn, the weather was unpleasant, and the seas were much rougher than during the first and second burns. Rolls averaged nearly 20 degrees to either side with a 30-degree maximum. All sampling and monitoring activities were accomplished according to plan. Several times the combustion effluent became visible as a plume for the first time during all three burns (except for those times when ammonia was injected into the stack) possibly because of high humidity from heavy rainfall. Winds were higher (averaging 12 to 14 m/sec, 24 to 28 knots) than during the previous two burns, so there were several instances when the plume partially eddied back onto the ship. During these periods the ship was put under power and oriented to avoid plume impingement.

Time averaged waste feed rates were not measured during the third burn. This was because of the rough weather, which prevented accurate gauging as tanks neared depletion, and to the tank rinsing procedure, which required waste tanks at near depletion to be filled with rinsing material. An overall waste feed rate was calculated from the total time of incineration and the volume of material burned.

In order to reduce TCDD-contaminated herbicide residuals in the waste tanks, a tank rinsing procedure was developed by the U.S. Air Force and approved by the U.S. EPA. During the third burn, waste tanks were rinsed serially as they were depleted by filling with TCDD-free herbicide. The TCDD-free rinsate (647.4 metric tons) had been loaded at Gulfport into Tank 2C and had not been incinerated during the first two burns. Used rinsate was incinerated at the end of the third burn, and the amount of rinsate was included in the third burn average feed rate.

During the first of the two scheduled stack sampling tests on 24 August, the purge air line to the on-line instrumentation broke, and the grab gas sample was not acquired. During this test the only operative hydrocarbon analyzer ceased functioning. Later it was found that the sample capillary to the flame detector had become plugged. The sample capillary from the inoperative HC analyzer was installed, but after a short operating period it too became plugged. Both HC analyzers were then inoperative. The two operable CO analyzers had problems, one tended to drift upwards in scale because of condensation in the sample cell, and the other instrument became too noisy to operate. On-line monitoring was limited to 1 hour per day because of these problems.

At the end of the first test, the brake on the traversing probe failed, and the probe moved part way into the stack. Coolant water was still flowing, and the probe, after removal from the stack, was found to be undamaged. When not actually in use, the probe was thereafter tied to the probe mount to preclude inadvertent insertion into the stack.

After docking at Johnston Island on 4 September, all TRW equipment was removed from the M/T Vulcanus for shipment back to the mainland.

3.3 MARINE MONITORING

Plankton samples were collected in the burn site before and after the first burn. The initial samples were collected near the eastern boundary of the site on 15 July 1977 before incineration was started. The first plankton tow was conducted 5 hours before sunrise and the second tow 4 to 5 hours after sunset.

After completing incineration of the first shipload of Herbicide Orange, plankton tows were made at least 64.3 km (40 mi) downwind of the site of last burning. The ship was allowed to drift during the post-burn tows. Plankton tows were conducted 4 to 5 hours after sunrise and 4 to 5 hours after sunset on 24 July. All plankton samples were placed in quart jars, labeled, and preserved with formalin for analysis by the U.S. EPA.

3.4 OTHER SAMPLES AND MEASUREMENTS

3.4.1 Workspace Air Monitors

Workspace air monitors consisted of four MSA personnel samplers stationed in the dining room, pump room, portable laboratory on the main deck, and incinerator room. A 3 mm ID glass tube, filled with Chromosorb 102® for a length of 25 mm, was attached to each sampler and used to sample air for 2,4-D and 2,4,5-T analysis. This technique for sampling air for 2,4-D and 2,4,5-T had been previously tested by USAF-OEHL.(2)

The practical life of a pump battery was 12 hours on one charge. The need for changing pumps was eliminated by using transformers (220V/110V) so the pumps could be operated by the ship's power. The monitor in the pump room could not be operated from a transformer because of maritime regulations. During the first burn, the tubes were changed every 12 hours. One the second and third burns the tubes were changed every 24 hours. Selected tubes were analyzed on Johnston Island after each burn, the remaining tubes have been archived.

3.4.2 Wipe Samples

Wipes of selected areas of the ship were made to monitor how effectively the boundary-isolation plan was keeping herbicide from living areas. Using 11-cm diameter Whatman 41® filter paper discs, areas about 1 square meter were wiped. The wipes were extracted with benzene, and the extracts were analyzed with the onboard gas chromatograph.

3.4.3 Air and Impinger Samples

Workspace air at various positions on the ship was sampled using 10 ml gas sampling syringes, and analyses were performed with the onboard gas chromatograph. In addition, samples of the benzene impingers were analyzed to determine concentrations of 2,4-D and 2,4,5-T in the combustion effluent.

3.4.4 Waste Feed Rate

The sealed waste gauging system installed for the Herbicide Orange burns was not satisfactory for measuring waste feed rates because it gauged only the top one-third of each tank. In addition, it could not compensate for the ship's rolling which caused tank contents to slosh. A manual method of gauging tank contents was also unsatisfactory because it could not compensate for the ship's rolling.

Waste feed rates were determined, therefore, by measuring the time to deplete each tank. The volume of each tank was known, and the amount of waste loaded into each tank was measured after loading. During incineration, the times required to pump out the tanks were measured. During the first burn, as described in Section 3.2, some of the tanks were not completely emptied. The contents of these tanks were gauged after returning to Johnston Island, and the feed rates were corrected for residual waste. On the second and third burns, the tanks were emptied to near dryness, which meant residuals of 20 to 50 liters according to the ship's Chief Engineer.

3.4.5 Temperature Measurements

Permit conditions required hourly notation of the temperatures of the controller and indicator thermocouples. The ship's engineering staff entered temperature readings in the log and made them available to test personnel. Once each day the flame temperature of each incinerator was measured with an optical pyrometer.

3.5 COMBUSTION EFFLUENT SAMPLES ACQUIRED

Samples acquired onboard the M/T Vulcanus relating to the combustion process were: heat-traced line rinses, probe rinses, sorbent traps, benzene impingers, composite feeds, grab gas bags, and burner residues. Probe rinses, heat-traced line rinses, sorbent traps, and benzene impingers were combustion effluent samples. Composite feed samples were necessary to calculate destruction efficiencies for the combustion process. Burner residue samples were acquired because they may be a waste disposal problem. On the M/T Vulcanus, however, burner residues were returned to the incinerator, so that they were neither a disposal problem nor an emission. Table 5 shows the dates of the tests, the sampling times, volumes of dry gas acquired, moisture content of the gas samples, average waste feed rates for each test, and the samples which were taken. Initially, it was intended to rinse the probe only once after each shipload was incinerated. It was decided after the first two tests during the first burn to rinse the probe after each test, if practicable; it was thought, as discussed in Section 3.2.1, that excess condensation might be occurring in the probe because of lower than desirable sample outlet gas temperatures.

The Lear-Siegler and USAF-OEHL sampling trains were operated simultaneously, pulling combustion effluent through the same probe and heat-traced line. One Lear-Siegler sample of about 4 m^3 and three impinger samples of about 0.1 m^3 each were acquired per test. Thus, a complete sorbent trap or impinger sample

TABLE 5. SUMMARY OF COMBUSTION EFFLUENT SAMPLES ACQUIRED

	First Burn						Second Burn					Third Burn	
Test Dates, 1977	7/14	7/15	7/16	7/18	7/19	7/23	8/7	8/8	8/10	8/13	8/14	8/24	8/28
Sampling Time, min	212	255	240	192	240	240	195	238	231	250	221	238	221
Volume Sampled, dry m^3	3.93	6.20	6.09	5.84	5.86	5.23	5.03	6.30	3.93	8.83	5.99	2.81	6.88
Volume % Moisture	6.9	+	10.4	+	+	+	+	+	+	6.9	+	+	8.4
Average Feed Rate, metric tons/hr*	6.05	6.05	7.03	7.46	6.99	7.28	6.85	6.85	7.38	7.16	6.91	7.60	5.90
Samples Taken:													
Composite Feed	x	x	x	x	x	x	x	x	x	x	x	x	x
Sorbent Trap	x	x	x	x	x	x	x	x	x	x	x	x	x
Line Rinse	x	x	x	x	x	x	x	x	x	x	x	x	x
Probe Rinse	±	±	x	±	x	x	x	x	x	x	x	x	x
Impingers	x	x	x	x	x	x	x	x	x	x	x	x	x
Silica Gel	x	x	x	x	x	x	x	x	x	x	x	±	x
Grab Gas	±	±	x	±	x	±	x	x	x	x	x	±	x
Burner Residue	±	±	±	±	±	x	±	x	±	±	x	±	±

*Metric tons per hour per incinerator.

+Samples from these tests were archived and not analyzed.

±Samples not acquired.

included a portion of the probe and heat-traced line rinses for that test. The apportionment of the probe and heat-traced line rinses was based on the amount of stack effluent acquired in a given sorbent trap or impinger sample. Thus, if a Lear-Siegler sorbent trap sample represented 94% of the total volume of effluent sampled, then 94% each of the probe and heat-traced line rinses for that test were taken as part of that Lear-Siegler train sample in order to obtain proper mass discharge rates.

Table 6 gives the total volume of effluent sampled in each test, volumes of each probe and heat-traced line rinse, volumes of effluent represented by each sorbent trap and impinger sample, and portions of each probe and heat-traced line rinse which are part of each sorbent trap and impinger sample.

3.6 SAMPLE NOMENCLATURE

The variety and number of samples acquired onboard the M/T Vulcanus necessitated a compact nomenclature. Table 7 lists the sample labeling scheme used on the ship and in the subsequent analyses. These sample designators are used in presenting analytical results. A typical sample name might be HO-1-ST-714-F. This designation means:

- HO - Herbicide Orange program
- 1 - First shipload (first burn)
- ST - Sorbent trap sample
- 714 - Date sample was taken, i.e., 7/14/77
- F - Fuel oil was being burned.

3.7 WASTE DESCRIPTION

In addition to Herbicide Orange, the waste incinerated contained diesel fuel, which was used to rinse drums and other equipment used in dedrumming and handling the herbicide, and water-contaminated herbicide. Table 8 lists physical properties(2) of Herbicide Orange. Table 9 lists properties(2) of the ingredient esters of Herbicide Orange. Table 10 lists properties(2) of TCDD. Table 11 shows the chemical composition of several lots of Herbicide Orange resulting from

TABLE 6. TRAIN SAMPLE VOLUMES AND APPORTIONMENT OF PROBE AND LINE RINSES

						Lear-Siegler Train				Wright State Impinger			
Burn	Date	Analyze Samples	Total Gas Volume m^{3+}	Probe Rinse Volume mℓ	Line Rinse Volume mℓ	Gas Volume m^3	%	Probe Rinse Split, mℓ	Line Rinse Split, mℓ	Gas Volume m^3	%	Probe Rinse Split, mℓ	Line Rinse Split, mℓ
1	7/14/77	Yes	4.2667		2280	3.9262	92.02	74.9	2098	0.1129	2.65	2.16	60.42
1	7/15/77	No	6.5703		2195	6.2012	94.38	11.9	2082	0.1240	1.89	2.37	41.49
1	7/16/77	Yes	6.4513		2320	6.0914	94.42	116	2191	0.1179	1.83	2.25	42.46
1	7/17/77		17.2883	330		16.2188	93.81	310		0.3548	2.05	6.77	
1	7/18/77	No	6.2105		2175	5.8449	94.11	146	2047	0.1161	1.87	2.90	40.67
1	7/19/77	No	6.2057		2385	5.8618	94.46	146	2253	0.1263	2.04	3.16	48.65
1	7/22/77		12.4162	310		11.7067	94.29	292		0.2424	1.95	6.06	
1	7/23/77	No	5.5708	340	1565	5.2380	94.03	320	1472	0.1142	2.05	6.97	32.08
2	8/7/77	No	5.7876	380	1290	5.0346	86.99	331	1122	0.2305	3.98	15.1	51.4
2	8/8/77	No	6.9367	380	2030	6.3016	90.84	345	1844	0.1962	2.83	10.7	57.4
2	8/10/77	No	4.6008	440	2980	3.9348	85.54	376	2549	0.2085	4.53	19.9	135.0
2	8/13/77	Yes	9.7710	440	1140	8.8333	90.40	398	1031	0.3249	3.33	14.6	37.9
2	8/14/77	No	6.5367	450	2285	5.9894	91.63	412	2094	0.1913	2.93	13.2	66.9
3	8/24/77	No	3.4951	423	1962	2.8136	80.5	341	1579	0.2247	6.43	27.2	126
3	8/28/77	Yes	7.6127	423	1642	6.8847	90.43	383	1485	0.2266	2.98	12.6	48.9

(continued)

*Sample calculation in Appendix F.1.

+Gas volumes have been corrected to 20^{o}C and 1013.2 mbar pressure.

TABLE 6. (continued)

						TRW Impinger				Battelle/USAF Impinger			
Burn	Date	Analyze Samples	Total Gas Volume m^{3+}	Probe Rinse Volume mℓ	Line Rinse Volume mℓ	Gas Volume m^3	%	Probe Rinse Split, mℓ	Line Rinse Split, mℓ	Gas Volume m^3	%	Probe Rinse Split, mℓ	Line Rinse Split, mℓ
1	7/14/77	Yes	4.2667		2280	0.1160	2.72	2.21	62.02	0.1116	2.62	2.13	59.74
1	7/15/77	No	6.5703		2195	0.1189	1.81	2.27	39.73	0.1262	1.92	2.41	42.14
1	7/16/77	Yes	6.4513		2320	0.1209	1.87	2.31	43.58	0.1211	1.88	2.31	43.62
1	7/17/77		17.2883	330		0.3558	2.06	6.79		0.3589	2.08	6.85	
1	7/18/77	No	6.2105		2175	0.1260	2.03	3.15	44.15	0.1235	1.99	3.08	43.28
1	7/19/77	No	6.2057		2385	0.1117	1.80	2.78	42.93	0.1059	1.71	2.65	40.78
1	7/22/77		12.4162	310		0.2377	1.91	5.93		0.2294	1.85	5.73	
1	7/23/77	No	5.5708	340	1565	0.1128	2.02	6.87	31.61	0.1058	1.90	6.46	29.74
2	8/7/77	No	5.7876	380	1290	0.2701	4.67	17.7	60.2	0.2524	4.36	16.6	56.3
2	8/8/77	No	6.9367	380	2030	0.2185	3.15	12.0	63.9	0.2210	3.19	12.2	64.8
2	8/10/77	No	4.6008	440	2980	0.2263	4.92	21.6	147.0	0.2304	5.01	22.0	149.0
2	8/13/77	Yes	9.7710	440	1140	0.334	3.42	15.0	39.0	0.2788	2.85	12.6	32.5
2	8/14/77	No	6.5367	450	2285	0.1774	2.71	12.2	61.9	0.1786	2.73	12.3	62.4
3	8/24/77	No	3.4951	423	1962	0.2305	6.6	27.9	129.0	0.2263	6.48	27.4	127
3	8/28/77	Yes	7.6127	423	1642	0.2203	2.89	12.2	47.5	0.2811	3.69	15.6	60.6

*Sample calculation in Appendix F.1.

+Gas volumes have been corrected to 20°C and 1013.2 mbar pressure.

TABLE 7. HERBICIDE ORANGE PROGRAM SAMPLE LABELING SCHEME

Program Name	Shipload	Sample Designator*	Start Date†	Nature of Sample	Location Where Sample Taken	Destination of Sample	Other Identifier
HO	1	ST		F (Fuel)	I (Incinerator)	T (TRW)	Miscellaneous
	2	BI		H (Herbicide)	G (Galley)	W (WSU)	
	3	CF		A (Acetone)	Q (Quarters)	B (BCL)	
		LR		B (Benzene)	C (Container)	S (Ship)	
		WS			S (Stack)		
		EP			P (Pump Room)		
		EW					
		AM					
		GG					
		BR					
		PR					
		SW					
		AS					
		SG					

*ST = Lear-Siegler sorbent trap
BI - USAF-OEHL benzene impinger
CF = Composite feed
LR = Heat traced line rinse
WS = Wipe sample
EP = EPA plankton sample
EW = EPA sea water sample
AM = Ambient monitor, Chromosorb 102® tubes
GG = Grab gas, Tedlar® bag
BR = Burner head residue
PR = Probe rinse
SW = Ship's water
AS = Air sample
SG = Silica gel

†Date of start of test, e.g., 28 July 1977 = 728.

multiple drum analyses. The data in this table were calculated from results given in Reference 6 and apply only to Gulfport stocks.

The permit for the second and third burns (U.S. EPA Special Permit No. 770DH001S) allowed other wastes, stored in old Herbicide Orange drums to be incinerated on the third burn provided that appropriate data were supplied to U.S. EPA and that subsequently their approval was granted. Table 12 lists pertinent data on drums of other wastes which were loaded for the third burn(7) and which were authorized for incineration.(7)

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6. B.M. Hughes, D.C. Fee, M.L. Taylor, T.O. Tiernan, C.E. Hill, Jr., and R.L.C. Wu, "Analytical Methodology for Herbicide Orange, Volume 1. Determination of Chemical Composition," from Tables XVI to XIX, pp. 73-79, Final Report to U.S. Air Force Systems Command, No. ARL TR 75-0110, May 1975.
7. Addendum to U.S. EPA Special Permit No. 770DH001S.

TABLE 8. GENERAL CHEMICAL AND PHYSICAL PROPERTIES of HERBICIDE ORANGE*

Property	Orange	Orange II
Heat Value	10,017 Btu/lb	+
Physical State	Liquid at room temperature	+
Color	Reddish brown to straw	+
Appearance	Dark, rust colored liquid of oily consistency	+
Solubility	Soluble in diesel fuel and most organic solvents. Insoluble in water.	+
Flash Point	146°C (295°F)	unknown
Specific Gravity, 25°C	1.275 to 1.295	1.220 - 1.242
Weight (lb/gal)		
Total ester at 20°C	10.7	10.2
Vapor Pressure (30°C)	3.6 x 10^{-4} mm Hg	+
Viscosity, centipoise		
20°C	46	+
30°C	24	+
Theoretical % Weight		
Carbon	49.[illegible]	59.12
Chlorine	29[illegible]	27.27
Oxygen	16.[illegible]	15.20
Hydrogen	4.65	5.41
Free Acid (by weight)	0.5% maximum	0.5% maximum
Corrosiveness	Noncorrosive to most metals. Deleterious to some paints, natural rubber, and neoprene. Teflon ®, Viton ®, polyethylene, and butyl rubber are resistant.	

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* Adapted from Reference 2.

+ These properties of Orange II were not determined.

TABLE 9. GENERAL PROPERTIES OF INGREDIENT ESTERS OF HERBICIDE ORANGE*

Property	N-Butyl-2,4-D	N-Butyl-2,4,5-T	Iso-Octyl-2,4,5-T
Purity (ester by weight)	98%, minimum	95%, minimum	95%, minimum
Appearance		— clear, reddish brown liquids —	
Free Acid (by weight)	0.5%, maximum	0.5%, maximum	0.5%, maximum
Specific Gravity (20°C)	+	1.316 - 1.340	1.200 - 1.22
Molecular Weight	277.15	311.60	367.71
Theoretical % Weight			
Carbon	52.01	46.26	52.26
Chlorine	25.58	34.13	28.93
Oxygen	17.32	15.40	13.05
Hydrogen	5.09	4.21	5.76

* Adapted from Reference 2.

+ Parameter not determined.

TABLE 10. GENERAL DATA RELATIVE TO TCDD*

Property	Data
Content in Orange or Orange II	Range: 0-47 mg/kg. Estimated mean is 1.9 mg/kg with 95% confidence limits of 2.6 and 1.2 mg/kg.
Molecular Weight	321.97
Theoretical % Weight	
Carbon	44.77
Chlorine	44.04
Oxygen	9.94
Hydrogen	1.25

*Adapted from Reference 2.

TABLE 11. AVERAGE COMPOSITION OF SEVERAL LOTS OF HERBICIDE ORANGE*

Compound	Average Concentration, %+			
	ASN 5	ASN 8	ASN 10	ASN 14
Butanol	1.7	0.96	0.3	0.78
Toluene	0.65	1.51	0.1	2.52
Xylenes, ethylbenzene	3.4	±	0.03	±
Butyl chloride	0.13	0.10	0.05	0.16
Dichlorophenol	0.34	0.23	0.12	0.31
Unknown, #	0.14	±	0.57	±
Unknown, #	±	±	0.57	±
Trichlorophenol	4.2	0.42	0.23	0.70
Dichloromethoxyanisole	0.16	±	±	±
Trichloroanisole	0.89	±	±	±
Dichloromethoxyanisole	0.21	±	±	±
Dichloromethoxyanisole	0.40	±	±	±
Butoxydichlorobenzene	±	±	0.16	±
Butoxytrichlorobenzene	±	±	0.16	±
Butyl monochlorophenoxyacetate	0.95	0.55	1.38	1.34
Butyl dichlorophenoxyacetate	0.16	±	2.77	0.90
Butyl dichlorophenoxyacetate	0.19	±	±	±
Butyl dichlorophenoxyacetate	0.23	±	±	±
Unknown, #	0.45	±	±	±
Butyl dichlorophenoxyacetate	42.4	41.7	49.1	43.2
Butyl trichlorophenoxyacetate	0.38	0.89	1.22	1.75
Butyl trichlorophenoxyacetate	39.5	38.9	43.4	41.0
Butyl methoxydichlorophenoxyacetate	2.9	5.76	2.68	5.89
Octyl dichlorophenoxyacetate	±	3.33	0.29	±
Octyl dichlorophenoxypropionate	±	0.33	±	±
Octyl trichlorophenoxyacetate	±	2.22	0.42	±
Octyl methoxydichlorophenoxyacetate	±	0.37	±	±
Unknown, #	0.1	±	±	±
Unknown, #	0.03	±	±	±
Butyl (bis-dichlorophenoxy) acetate	0.16	0.38	0.42	0.47
Butyl (bis-trichlorophenoxy) acetate	±	1.8	±	±
Butyl (methoxydichlorophenoxy)-trichlorophenoxyacetate	±	0.21	±	±
TCDD, µg/g	0.15	<0.02	0.26	<0.02

*These data were adapted from Reference 6 and apply to Gulfport stocks only.

+ASN means analytical sequence number, an arbitrary designator for various lots.

±Compound not detected. Detection limit was 0.1%.

#Identity unknown because of lack of match between sample and reference spectra.

TABLE 12. DRUMS AUTHORIZED FOR LOADING FOR THIRD BURN

Drum Identification	Primary Constituent	Arsenic Content, ppm	Remarks
X-112	Herb. Orange	N.D.	Load in Center Tanks
X-113	Herb. Orange/Water	120 (2200 in 3/4" Water)	Load in Center Tanks
X-136	Herb. Orange	N.D.	Load in Center Tanks
X-128	Water on Herb. Orange	N.D.	Load in Center Tanks
X-135	Motor Oil	N.D.	Load in Center Tanks
X-130	Herb. Orange	N.D.	Load in Center Tanks
X-131	Herb. Orange	612	Load in Center Tanks
X-132	Herb. Orange	476	Load in Center Tanks
X-126	Used Motor Oil	N.D. P6 = 100 mg/l	Load in Center Tanks
X-127	Herb. Orange	516	Load in Center Tanks
X-110	Herb. White*	20	Load in Center Tanks
X-111	Herb. Orange	412	Load in Center Tanks
X-116	Herb. Orange and White*	31	Load in Center Tanks
X-102	Water	N.D.	Load in Tank 6P
X-104	Herb. White*	20	Load in Center Tanks
X-105	Herb. White*	N.D.	Load in Center Tanks
X-106	Herb. White*	N.D.	Load in Center Tanks
X-108	Water	N.D.	Load in Tank 6P
X-109	Herb. White*	QNS	Load in Center Tanks
X-114	Herb. White*	N.D.	Load in Center Tanks
X-117	Diesel Fuel	N.D.	Load in Center Tanks
X-115	Diesel Fuel	N.D.	Load in Center Tanks
X-118	Herb. White	N.D.	Load in Center Tanks
X-121	Diesel Fuel	N.D.	Load in Center Tanks
X-133	Water Over Herb. White*	N.D.	Load in Center Tanks
X-100	Herb. Orange	112	Load in Center Tanks
X-129	Herb. Orange and Oil	N.D.	Load in Center Tanks
X-134	1/4" Water Over Orange	N.D.	Load in Center Tanks
X-123	6" Water Over Orange	20 (27 in Water)	Load in Center Tanks
X-122	Herb. Orange, Green Dye	N.D.	Load in Center Tanks
X-119	Herb. White*	N.D.	Load in Center Tanks
T-1	6" Water Over Orange	---	Load in Center Tanks
T-5	1/4" Water Over Orange	---	Load in Center Tanks
T-10	Water	---	Load Tank 6P

N.D. = None Detected QNS = Quantity not sufficient for analysis

*Herbicide White was a mixture of Picloram and 2,4-D.

4. TEST RESULTS

This section presents the results of monitoring, sampling, and analysis operations on this program. Many of the calculations are complex; therefore, sample calculations are presented in Appendix F. When an example calculation is given, the text is so noted.

4.1 OPERATIONAL AND FIELD DATA

Data acquired onboard the ship during the three burn periods included on-line gas composition, waste feed rates, and incinerator wall and flame temperatures. Each of these is discussed in the following sections.

4.1.1 Combustion Effluent Gas Composition

Signal outputs from the on-line instruments were recorded on strip charts and an Esterline-Angus data logging device which automatically printed out the millivolt signal from each instrument at 5-minute intervals. Data were acquired for approximately 29 hours during the first 10-day burn period, and for 17 hours and 13 hours, respectively, during the second and third burns of 11 days each. Monitoring times ranged from 1 to 5 hours duration representing random and preselected day and night monitoring. Daylight monitoring was normally coordinated with stack sampling activities so that on-line data may be compared to results derived from the analysis of stack gas samples. During the on-line monitoring, the data were continuously evaluated and assessed daily to determine compliance with combustion efficiency, temperature, and excess air requirements specified in the permit.

Results of the gas composition analyses for each burn, shown in Tables 13, 14 and 15, were calculated on a dry basis, i.e., the samples were water-free when analyzed and no correction has been made for removed moisture. Oxygen values have been corrected for the volumes of CO_2 and HCl which were removed from the oxygen analyzer sample feed before analysis by a scrubber installed to protect the instrument. The range of levels for each species shows the

TABLE 13. GAS COMPOSITION DATA - FIRST BURN

Day No.	Date		O_2 (percent)	CO_2 (percent)	CO (ppm)	HC[a] (ppm)	HCl[b] (percent)	N_2[c] (percent)	Combustion[d] Efficiency	Excess Air[e] (percent)
1[f]	7/14	Range	10.2-13.7	2.8-8.4	2-8	7-20			99.979-99.997	
		Mean	12.9	4.3	4	11	0[f]	82.8	99.99	144
1	7/14	Range	5.6-8.6	9.4-11.8	2-7	37-130			99.993-99.998	
		Mean	8.4	10.4	5	92	2.2	79.0	99.99	67
2	7/15	Range	7.3-12.8	9.7-11.8	1-8	21-52			99.993-99.999	
		Mean	8.1	10.7	5	32	2.2	79.0	99.99	63
3	7/16	Range	8.0-9.5	8.1-11.6	3-8	7-9			99.993-99.997	
		Mean	8.4	10.5	5	8	2.2	78.9	99.99	68
4	7/17	Range	8.1-10.0	9.9-10.6	4-15	-[g]			99.986-99.996	
		Mean	8.4	10.3	8		2.1	79.2	99.99	67
5	7/18	Range	7.2-8.9	8.3-12.7	1-15	-[g]			99.986-99.999	
		Mean	7.9	11.0	7		2.3	78.8	99.99	61
6	7/19	Range	7.5-10.5	8.8-12.6	2-12	-[g]			99.987-99.998	
		Mean	8.5	10.5	8		2.2	78.8	99.99	69
7	7/20	Range	8.2-10.1	7.4-11.5	3-14	7-57			99.986-99.997	
		Mean	9.1	9.9	7	22	2.0	79.0	99.99	77
8	7/21	Range	7.9-8.4	9.6-10.9	8-17	10-14			99.984-99.992	
		Mean	8.3	10.1	12	12	2.1	79.6	99.99	65
10	7/23	Range	8.1-8.8	9.3-10.2	9-19	6-22			99.981-99.991	
		Mean	8.1	10.0	14	14	2.1	79.8	99.99	62

a) As methane
b) Appendix F.2
c) By difference
d) Appendix F.2
e) Appendix F.2
f) Fuel oil background test
g) No data. HC analyzer was inoperative.

TABLE 14. GAS COMPOSITION DATA - SECOND BURN

Day No.	Date		O_2 (percent)	CO_2 (percent)	CO (ppm)	HC[a] (ppm)	HCl[b] (percent)	N_2[c] (percent)	Combustion[d] Efficiency	Excess Air[e] (percent)
1[f]	8/6	Range	7.7-11.0	6.5-9.5	3-5	3-6			99.993-99.997	
		Mean	9.7	7.8	4	4	0[f]	82.5	99.99	80
1	8/6	Range	8.5-10.5	8.8-10.7	6-11	4-7			99.990-99.993	
		Mean	9.4	9.7	8	6	2.0	78.9	99.99	82
2	8/7	Range	5.9-6.9	12.2-13.9	5-9	2-11			99.993-99.996	
		Mean	6.4	13.0	8	9	2.7	77.9	99.99	45
3	8/8	Range	6.8-8.5	10.4-11.7	4-8	7-11			99.992-99.996	
		Mean	7.9	11.1	6	9	2.3	78.7	99.99	61
4	8/9	Range	6.5-7.7	10.3-11.0	5-10	19-31			99.991-99.996	
		Mean	7.2	10.6	8	26	2.2	80.0	99.99	52
5	8/10	Range	8.1-11.1	9.1-11.2	3-19	12-20			99.982-99.997	
		Mean	9.3	10.1	11	16	2.1	78.5	99.99	81
8	8/13	Range	8.7-12.3	6.9-11.0	3-12	7-23			99.985-99.996	
		Mean	9.8	9.1	8	16	1.9	79.2	99.99	88
9	8/14	Range	7.1-10.2	10.4-13.2	11-25	-[g]			99.978-99.989	
		Mean	8.4	11.5	19		2.4	77.7	99.98	69
10	8/15	Range	9.0-10.6	6.7-10.0	9-19	-[g]			99.975-99.990	
		Mean	9.8	8.7	11		1.8	79.7	99.98	87
11	8/16	Range	9.0-12.8	7.0-9.7	7-10	-[g]			99.987-99.991	
		Mean	10.6	7.8	9		1.6	80.0	99.99	101

a) As methane
b) Appendix F.2
c) By difference
d) Appendix F.2
e) Appendix F.2
f) Fuel oil background test
g) No data. HC analyzer was inoperative.

TABLE 15. GAS COMPOSITION DATA - THIRD BURN

Day No.	Date		O_2 (percent)	CO_2 (percent)	CO (ppm)	HC(a) (ppm)	HCl(b) (percent)	N_2(c) (percent)	Combustion(d) Efficiency	Excess Air(e) (percent)
1(f)	8/24	Range Mean	9.7-14.5 12.1	9.9-10.0 10.0	10-11 11	-(g)	0(f)	77.9	99.989-99.989 99.99	143
1	8/24	Range Mean	8.2-11.6 9.3	9.9-12.0 11.1	10-13 11	-(g)	2.3	77.3	99.989-99.990 99.99	84
2	8/25	Range Mean	5.4-10.0 8.9	9.4-15.1 10.9	13-25 18	-(g)	2.3	77.9	99.978-99.989 99.98	76
3	8/26	Range Mean	6.5-11.5 9.4	7.2-12.6 9.6	6-30 21	-(g)	2.0	79.0	99.968-99.993 99.98	82
4	8/27	Range Mean	5.8-8.8 7.5	9.7-14.7 12.0	12-29 25	-(g)	2.5	78.0	99.975-99.987 99.98	57
6	8/29	Range Mean	8.3-10.2 9.5	9.7-13.0 11.2	14-22 19	-(g)	2.3	77.0	99.978-99.987 99.98	88
7	8/30	Range Mean	8.8-9.6 9.4	10.3-12.8 11.3	14-24 20	-(g)	2.3	77.0	99.980-99.987 99.98	86
8	8/31	Range Mean	8.9-9.6 9.1	10.2-11.4 10.1	18-25 21	-(g)	2.1	78.7	99.978-99.985 99.98	78
9	9/1	Range Mean	9.0-10.5 9.6	10.0-11.6 10.7	6-11 8	-(g)	2.2	77.5	99.990-99.994 99.99	88
10	9/2	Range Mean	8.1-10.8 9.4	10.0-12.3 11.1	16-28 23	-(g)	2.3	77.2	99.976-99.986 99.98	86
11	9/3	Range Mean	7.2-9.3 8.2	12.0-14.0 12.9	14-26 22	-(g)	2.7	76.2	99.979-99.988 99.98	69

a) As methane
b) Appendix F.2
c) By difference
d) Appendix F.2
e) Appendix F.2
f) Fuel oil background test
g) No data. HC analyzer was inoperative.

maximum and minimum levels measured for all data points. The mean value is a numerical average of all data points. Sample calculations for HCl concentration, combustion efficiency, and excess air are given in Appendix F.2.

Table 16 is a summary of the on-line data for all three burns. These data show the relative uniformity of the burning operation as evidenced by the low standard deviation in the stack concentrations of CO, CO_2, O_2, and total hydrocarbons. Based on the data obtained during incineration onboard the M/T Vulcanus, the combustion efficiency was 99.97% or greater during all monitoring periods. Excess air ranged from 45 to 101%, and the average oxygen concentration ranged from 5.4 to 12.8% for all Herbicide Orange burn data. For the fuel oil background tests, excess air varied from 80 to 144%.

On-line gas composition data were taken during a traverse of the sampling probe across the starboard incinerator stack. Data acquired at 1-minute intervals while the probe was stationary at each location are presented in Figure 15. Results indicate that incinerator combustion efficiency can be measured accurately with a fixed probe at any position greater than 10 cm into the furnace. All CO/CO_2 measurements beyond this point yielded calculated efficiencies of 99.991 ±0.002%.

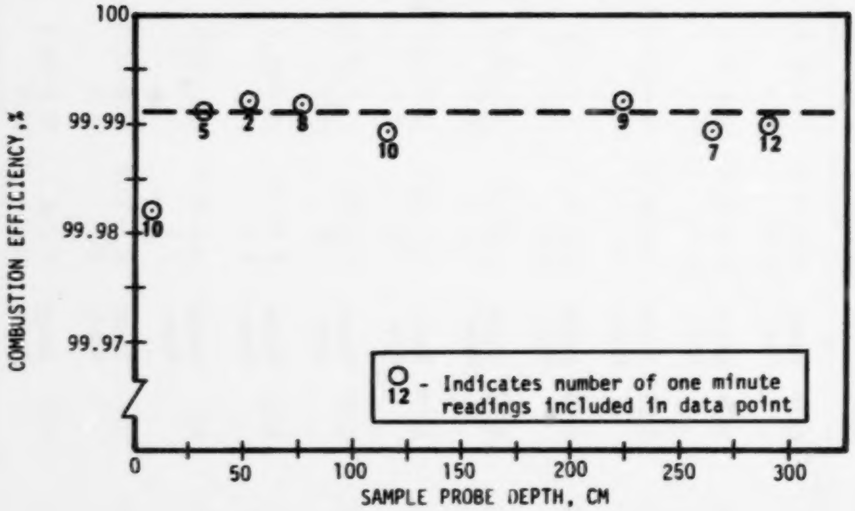

Figure 15. Combustion efficiency versus probe insertion depth.

TABLE 16. GAS COMPOSITION DATA SUMMARY — ALL HERBICIDE ORANGE BURNS

		O_2 (percent)	CO_2 (percent)	CO (ppm)	HC (ppm)	Combustion Efficiency (%)
Burn 1	Minimum	5.6	7.4	1	6	99.981
	Maximum	12.8	12.7	19	130	99.999
	Mean	8.7	10.1	8	30	99.992
	Standard Deviation	±1.4	±1.7	±3	±28	±0.004
	No. of Data Points	305	305	305	143*	305
Burn 2	Minimum	5.9	6.7	3	2	99.975
	Maximum	12.8	13.9	25	31	99.997
	Mean	9.1	10.1	11	14	99.989
	Standard Deviation	±1.4	±1.6	±5	±7	±0.005
	No. of Data Points	131	131	131	58*	131
Burn 3	Minimum	5.4	7.2	6	-*	99.968
	Maximum	12.6	15.1	30	-	99.994
	Mean	9.1	11.1	19	-	99.983
	Standard Deviation	±1.4	±1.6	±6	-	±0.006
	No. of Data Points	82	82	82	-	82
Combined Burns 1, 2, and 3	Minimum	5.4	6.7	1	2	99.968
	Maximum	12.8	15.1	30	130	99.999
	Mean	8.9	10.3	10	25	99.990
	Standard Deviation	±1.4	±1.7	±6	±25	±0.005
	No. of Data Points	518	518	518	201*	518

*HC Analyzer was inoperative for some tests during Burns 1 and 2 and for all of Burn 3.

4.1.2 Waste Feed Rate

Time averaged feed rates were recorded by tank during the first and second burns. Tables 17 and 18 present these data, giving burn times, volumes and weights of material burned, and burn rates in metric tons per hour. During the third burn, rough seas precluded measuring tank residuals (Section 3.2.3), so that incremental burn rates were not recorded. The average feed rate for the third burn was 15.2 metric tons per hour (3706 metric tons, 3114 m^3, in 244 hours). The overall amount of material incinerated during the third burn included 86.7 metric tons (85 m^3) of herbicide contaminated water and 647.4 metric tons (544 m^3) of TCDD-free herbicide that was used to rinse the waste tanks.

Specific gravities of five samples (Table 5) of first-burn herbicide were measured by WSU. These averaged 1.17 g/cm^3. WSU also measured the specific gravity of samples from the second and third burns, and both had specific gravities of 1.19 g/cm^3. These specific gravities were used to convert volumes of herbicide burned to mass flow rates.

4.1.3 Temperature and Residence Time

Both direct flame and wall temperature thermocouple measurements were made during incinerator operation. Wall thermocouple temperatures (controller and indicator thermocouples) were recorded hourly by the ship's crew for both of the incinerators. Independent flame temperature measurements were measured daily using a visible light optical pyrometer manufactured by Leeds & Northrop (Catalog No. 8632-F). Average daily flame and wall temperatures measured together with standard deviations during Herbicide Orange incineration are presented in Tables 19, 20, and 21 for each burn period.

These data indicate that the incinerator temperatures were consistently uniform and comparable. The low variation in the temperature measurements, particularly the flame temperatures, correlates well with the relatively constant combustion efficiencies derived from the on-line data and indicates well-controlled combustion during each burn.

TABLE 17. TANK BURNING SUMMARY — FIRST BURN

Tank No.*	Start		Finish		Time (hr)	Volume Loaded (m^3)	Volume Left (m^3)	Weight Burned (mt)#	Average Burn Rate (mt/hr)
	Day	Hour	Day	Hour					
1C	7/14	1600	7/16	0830	40.50	419.2	0.5	489.9	12.10
5C	7/16	0830	7/17	1830	34.00	415.7	7.1	478.1	14.06
3C	7/17	1830	7/19	0200	31.50	401.4	0	469.6	14.91
4C	7/19	0200	7/20	1000	32.00	424.8	44.9	444.5	13.89
2 P/S	7/20	1000	7/21	0720	21.33	264.8	0	309.8	14.52
3 P/S	7/21	0720	7/22	0230	19.17	240.8	0.7	280.9	14.65
4 P/S	7/22	0230	7/23	0255	24.42	308.3	3.1	357.0	14.62
5 P/S	7/23	0255	7/23	2225	19.50	242.7	0	284.0	14.56
6P	7/23	2225	7/24	0725	9.00	112.0	1.2	129.6	14.40
Total Burn	7/14	1600	7/24	0725	231.42	2829.7	57.5	3243.4	14.02

*C = center tank, P = port tank, S = starboard tank, P/S = both port and starboard tanks

#Average specific gravity for first burn waste was 1.17 g/cm^3 as determined by WSU.

TABLE 18. TANK BURNING SUMMARY - SECOND BURN

Tank No.*	Start Day	Start Hour	Finish Day	Finish Hour	Time (hr)	Volume Burned (m^3)	Weight Burned (mt)†	Average Burn Rate (mt/hr)
3C‡	8/6	2200	8/7	0445	‡	‡	‡	‡
1C	8/7	0445	8/8	1900	38.25	440.0	523.6	13.69
3C#	8/8	1900	8/9	2045	32.50#	404.0	480.8	14.79
2 P/S	8/9	2045	8/10	1800	21.25	264.8	315.1	14.83
5C	8/10	1800	8/12	0430	34.50	428.0	509.3	14.76
6P	8/12	0430	8/12	1330	9.00	116.0	138.0	15.34
3S	8/12	1330	8/12	2330	10.00	120.4	143.3	14.33
4C‡	8/12	2330	8/13	0530	‡	‡	‡	‡
3P	8/13	0530	8/13	1530	10.00	120.4	143.3	14.33
4C#	8/13	1530	8/14	2130	36.00#	440.0	523.6	14.54
4 P/S	8/14	2130	8/16	0000	26.50	307.8	366.3	13.82
5 P/S	8/16	0000	8/16	2040	20.67	242.6	288.7	13.97
Total Burn	8/6	2200	8/16	2040	238.67	2884.0	3432.0	14.38

*C = center tank, P = port tank, S = starboard tank, P/S = both port and starboard tanks.

†Specify gravity of second and third burn wastes was 1.19 g/cm^3 as determined by WSU.

‡Did not run tank to depletion at this time.

#Includes previous run time on this tank.

TABLE 19. INCINERATOR TEMPERATURES – FIRST BURN

	Starboard Furnace					Port Furnace				
	Indicator		Controller		Flame	Indicator		Controller		Flame
Date	$\bar{x}$(°C)	σ(°C)	$\bar{x}$(°C)	σ(°C)	(°C)	$\bar{x}$(°C)	σ(°C)	$\bar{x}$(°C)	σ(°C)	(°C)
7/14	1115	16	1225	19	1375	1109	6	1141	12	1375
7/15	1179	24	1280	32	1566	1166	31	1197	44	1493
7/16	1212	5	1311	16	1504	1203	7	1236	14	1510
7/17	1218	8	1319	30	1610	1214	18	1252	31	1576
7/18	1206	8	1287	26	1504	1226	11	1265	21	1427
7/19	1190	12	1275	23	1554	1222	15	1258	27	1516
7/20	1178	11	1261	24	1488	1203	14	1226	24	1488
7/21	1190	9	1283	22	1565	1216	23	1254	37	1493
7/22	1202	8	1299	18	1510	1202	32	1229	41	1566
7/23	1200	7	1279	17	1566	1191	20	1215	35	1504
7/24	1186	6	1254	35		1209	14	1244	31	

TABLE 20. INCINERATOR TEMPERATURES – SECOND BURN

	Starboard Furnace					Port Furnace				
	Indicator		Controller		Flame	Indicator		Controller		Flame
Date	$\bar{x}$(°C)	σ(°C)	$\bar{x}$(°C)	σ(°C)	(°C)	$\bar{x}$(°C)	σ(°C)	$\bar{x}$(°C)	σ(°C)	(°C)
8/7	1184	42	1340	34	1475	1203	25	1267	42	1488
8/8	1215	16	1294	42	1410	1230	15	1289	27	1477
8/9	1226	16	1310	43	1543	1234	8	1292	25	1482
8/10	1220	28	1263	49	1496	1240	12	1266	28	1493
8/11	1212	13	1318	45	1478	1234	9	1292	16	1455
8/12	1216	16	1309	47	1499	1225	14	1277	34	1488
8/13	1191	7	1260	28	1510	1208	10	1245	26	1485
8/14	1198	9	1271	32	1549	1213	7	1252	21	1482
8/15	1182	18	1257	54	1471	1194	19	1214	34	1438
8/16	1200	28	1267	62	1510	1202	8	1245	20	1518

TABLE 21. INCINERATOR TEMPERATURES — THIRD BURN

	Starboard Furnace					Port Furnace				
	Indicator		Controller		Flame	Indicator		Controller		Flame
Date	$\bar{x}$(°C)	σ(°C)	$\bar{x}$(°C)	σ(°C)	(°C)	$\bar{x}$(°C)	σ(°C)	$\bar{x}$(°C)	σ(°C)	(°C)
8/25	1181	14	1273	38	1427	1212	12	1265	19	1499
8/26	1195	9	1294	40	1574	1198	22	1227	41	1385
8/27	1207	15	1310	43	1493	1209	11	1257	25	1485
8/28	1177	16	1262	48	1493	1193	22	1231	56	1460
8/29	1190	20	1288	46	1510	1251	30	1325	47	1529
8/30	1203	20	1298	52	1471	1234	15	1292	28	1482
8/31	1199	10	1300	36	1471	1238	23	1313	42	1510
9/1	1191	17	1277	44	1454	1236	35	1303	62	1524
9/2	1199	24	1283	51	1526	1200	18	1254	38	1460

The incineration permits required that during startup (1) Herbicide Orange could not be fed until flame temperatures had reached 1280°C, (2) only one burner at a time could be switched from fuel oil to herbicide, and (3) flame temperatures of 1280°C had to be reached before the next burner was changed to herbicide. During the startup period of each burn, flame temperatures were measured with the optical pyrometer. Flame temperatures were always in excess of 1280°C as the burners were changed one-by-one to herbicide.

Based on the elemental composition of the waste (Table 8) and an average feed rate of 7.3 metric tons per hour per incinerator, the average emission rates of major stack gas components from each incinerator were calculated (Appendix F.3) to be:

CO_2	6,690 m^3/hr
HCl	1,378 m^3/hr
O_2	5,781 m^3/hr
N_2	47,150 m^3/hr
H_2O	4,839 m^3/hr

for a total average combustion effluent flow rate of 65,838 m^3/hr at 0°C.

Incinerator residence time was calculated from:

$$t = \frac{120}{\frac{65,838}{3600} \times \frac{T}{273.16}} \text{ sec}$$

where 120 is the volume of an incinerator in m^3; 65,838 is the average calculated combustion effluent flow rate in m^3/hr at 0^oC; and T is the flame temperature in ^oK. Incinerator residence times at different flame temperatures (Appendix F-4) are given below:

Flame Temperature (^oC)	Residence Time (sec)
1100	1.31
1200	1.22
1300	1.14
1400	1.07
1500	1.01

4.2 ANALYTICAL RESULTS

The results of laboratory analyses by TRW, WSU, and BCL of samples taken during the Herbicide Orange program are presented and discussed in this section. The purpose and scope of laboratory analyses performed by the three contractors were quite different. The TRW combustion effluent analyses were intended primarily to assure permit conditions were met.

Wright State University analyzed the combustion effluent samples for TCDD only. The results of their analyses for TCDD were used in deciding to issue a Special Permit for the second and third burns and to assess the overall acceptability of the incineration based on the destruction efficiency for TCDD.

Battelle-Columbus analyzed benzene impinger samples for 2,4-D and 2,4,5-T in order to give rapid confirmation of shipboard analyses. BCL also analyzed workspace air monitor samples and ship's drinking water samples for 2,4-D and 2,4,5-T.

The analytical methodology used by each of the three contractors is described briefly in this section.

4.2.1 Detection Limits

It will be seen later in this section that incineration of Herbicide Orange was quite effective. Neither 2,4-D nor 2,4,5-T was found in any combustion effluent sample. The definition and usage of detection limits are thus of importance in presenting the results of the analyses and in calculating destruction efficiencies.

A detection limit is that amount of sought-for substance (analyte) which gives a detectable signal. There are various definitions of what constitutes a detectable signal; in the GC and GC/MS analyses in this program, a peak height three times the noise level is considered detectable. Quantitation at the detection limit is marginal (± factor of 2-3) because the signal is not much larger than the noise.

The minimum detectable quantity may be defined as that amount of analyte which produces a signal which is quantitatable with some specified level of precision. The precision of quantitation at the minimum detectable quantity is usually greater than at the detection limit.

If the analyte is not detected, it may still be present in the sample but in an amount that does not produce a detectable signal. If the detection limit is adequate for the purposes of the analysis, it is used to set an upper bound on the analyte concentration which is indicated as less than (<) the value of the detection limit.

4.2.2 TRW Analytical Methodology

The TRW analyses employed a variety of techniques to develop estimates of the amounts and kinds of organic compounds emitted during the incineration process. The analytical scheme was a modified U.S. EPA Level I approach.(8,9) Figure 16 is a flow chart of the analytical scheme. A brief description is given below. Detailed procedures are given in Appendix C.

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8. "IERL-RTP Procedures Manual: Level 1 Environmental Assessment," U.S. EPA Document No. EPA-600/2-76-160a, June 1976.

9. "Combustion Source Assessment. Methods and Procedures Manual for Sampling and Analysis," TRW Report to U.S. EPA, September 1977.

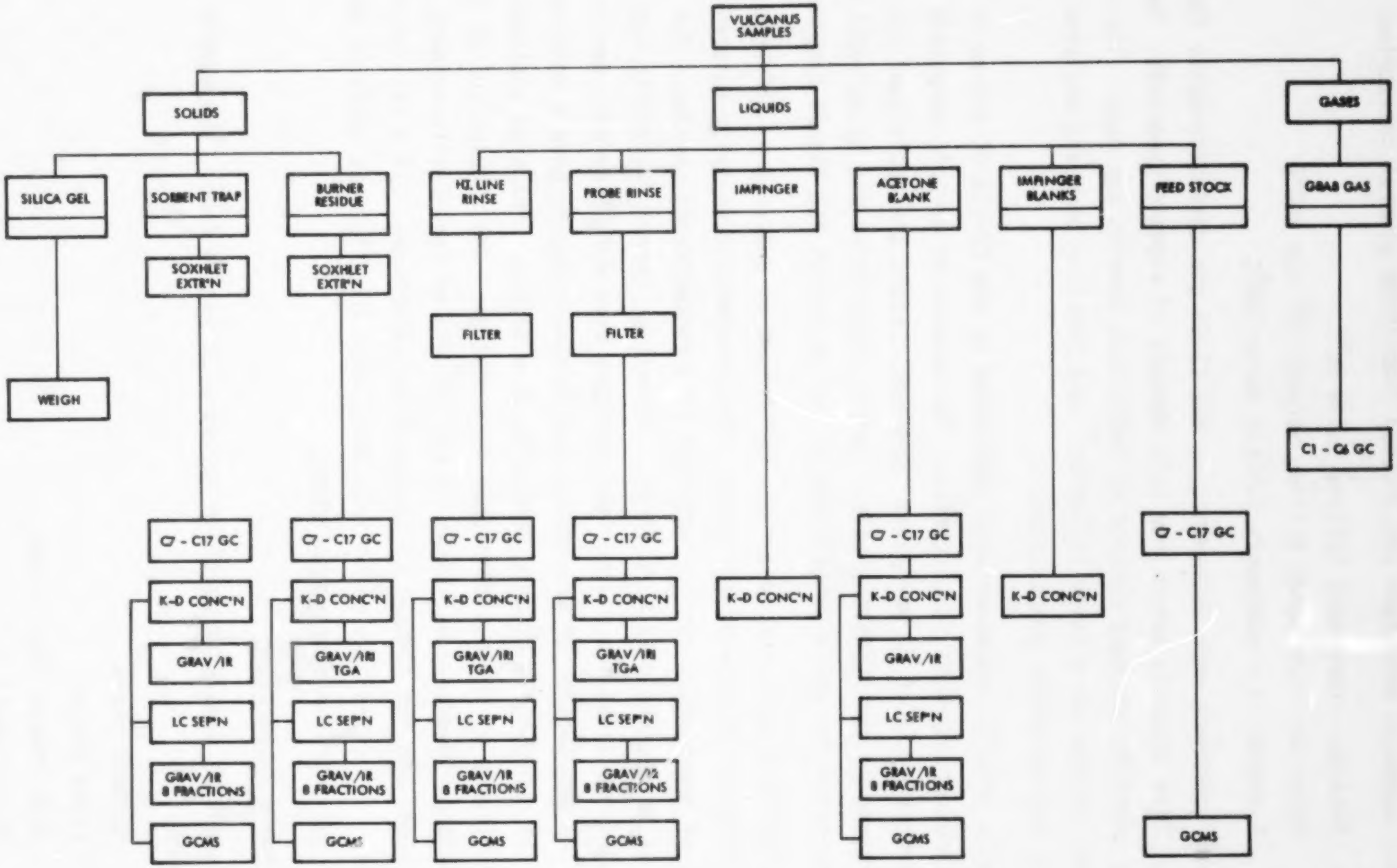
VULCANUS SAMPLES
SOLIDS
LIQUIDS
GASES
SILICA GEL
SORBENT TRAP
BURNER RESIDUE
HZ. LINE RINSE
PROBE RINSE
IMPINGER
ACETONE BLANK
IMPINGER BLANKS
FEED STOCK
GRAB GAS
WEIGH
SOXHLET EXTR'N
SOXHLET EXTR'N
FILTER
FILTER
C1 - C6 GC
C7 - C17 GC
K-D CONC'N
GRAV/IR
GRAV/IR TGA
LC SEP'N
GRAV/IR 8 FRACTIONS
GCMS

Figure 16. Flow diagram of TRW analysis plan.

Organic compound emissions are grouped into three general categories:

- Gaseous - compounds boiling below 90°C
- Volatile - compounds boiling between 90° and 300°C
- Nonvolatile - compounds boiling above 300°C

Gaseous compounds were determined by the C1-C6 gas chromatographic (GC) procedure. This analysis determined only amounts of organic compounds. No attempt to identify compound classes or individual species was made. The samples in this program were taken in Tedlar® gas sampling bags and analyzed at TRW. There was no sample preparation.

Volatile organic compounds were determined by the C7-C16 GC procedure and by gas chromatography-mass spectrometry. The amounts of organic compounds were determined by the C7-C16 GC analysis. Compound classes and individual species were determined by the GC/MS analysis. Sample preparation was by extraction and concentration for solid samples and by concentration for liquid samples.

Nonvolatile organic compounds were determined by gravimetry, infrared spectrophotometry, and thermogravimetry. The gravimetric analysis determines the weight of nonvolatile residue obtained from concentrated samples. For this program, the residue weights were large. Therefore, thermogravimetric analyses were performed to determine whether the residues were wholly or only partially organic. The combination of gravimetry and thermogravimetry gave a measure of the amount of nonvolatile organic compounds in a sample. Infrared analyses identified classes of organic compounds in a residue. The combination of the three techniques thus gave estimates of the amounts of nonvolatile organic compound emissions and the classes of compounds being emitted. If a residue was large, it was separated into eight fractions, each of which was analyzed by gravimetry and infrared spectrophotometry.

4.2.2.1 Sample Preparation

The extent of sample preparation varied with sample type. The sample types acquired were:

- Sorbent traps
- Probe rinses
- Heat traced line rinses
- Burner residues

- Composite feeds
- Grab gas in gas sampling bags
- Benzene impingers

The sorbent traps contain XAD-2, a porous polymer sorbent. The resin from each trap was extracted in a soxhlet extractor with pentane for 24 hours. The extract was then made to constant volume. Weighed portions of the burner residues were treated in the same manner. The probe and heat-traced line rinse samples were acetone solutions which also contained aqueous HCl, dissolved stainless steel, and firebrick particulates shed by the incinerator linings. Because of the large amount of such particulate material, the second and third burn probe and heat traced line rinses were filtered first through Whatman 41® filters and then through 47 micrometer cutoff Millipore® filters. The volumes of the probe and heat-traced line rinses were measured at Johnston Island after each burn before shipment. The volumes were also measured prior to starting the analyses.

Two-ml aliquots of the sorbent trap and burner residue extracts were set aside for the C7-C16 GC analysis. The remainder of the extracts were concentrated to 2 ml. Similarly, 250-ml portions of the probe and heat-traced line rinses were taken for analysis. A 2-ml aliquot of each was set aside for the C7-C16 GC analysis, and the remaining 248-ml portions were concentrated to 2 ml.

4.2.2.2 Analytical Techniques

Brief descriptions of the analytical techniques used are given below:

- Gravimetry/Infrared Spectroscopy (Grav/IR): A 0.5-ml aliquot of each concentrate was evaporated to constant weight, and the nonvolatile residue weight was measured. This weight provided an estimate of the content of nonvolatile organic compounds in a sample. An infrared spectrum was measured on a portion of each residue to give qualitative information on classes of compounds present in the sample.

- Thermogravimetric Analysis (TGA): Despite having been filtered, the residues from the probe and heat-traced line rinses were higher than usually observed. It was suspected that the residues might have significant inorganic contents. Therefore, thermogravimetric analyses were performed. Basically, the analysis involves heating the sample at a uniform rate and recording weight loss as a function of temperature. The sample is contained in a small pan suspended from a microbalance. The furnace atmosphere was nitrogen, so that only organic carbon was volatilized.

- C7-C16 Gas Chromatography: This analysis gives an estimate of the volatile organic content of a sample: compounds boiling between 90° and 300°C. The compounds in a neat sample or unconcentrated sample extract are separated in order of increasing boiling points. Compounds in various ranges, defined in calibration with the n-C7 through n-C16 alkanes, are quantitated as n-decane.

- Liquid Chromatographic Separation (LC): If an extract contains sufficient organic material that an emission concentration is calculated to exceed 0.5 mg/m^3 (or 0.1 mg/kg), then a portion of the extract is separated into eight fractions by liquid chromatography. This separation has the effect of simplifying the sample because each fraction will contain certain classes of compounds. Each fraction is evaporated to dryness. The residue weight is measured. An infrared spectrum is measured on each residue having sufficient weight.

- Gas Chromatography - Mass Spectrometry (GC/MS): In this technique, compounds in a concentrate are separated by gas chromatography and detected by a mass spectrometer. The mass spectrum of a compound is unique. In practice, the spectra of closely related positional isomers and optical isomers are not distinguishable. GC/MS is not particularly quantitative unless standards of each sought-for compound are also available and analyzed. In the analysis of the herbicide samples, quantitative measurements were made for 2,4-D and 2,4,5-T. Estimates of concentrations of other identified compounds were also made.

4.2.3 TRW Analytical Results

4.2.3.1 Waste Feed Analyses

Four composite feed samples, taken at Burner No. 4, were analyzed. One was a sample of the diesel fuel used to heat the incinerators and was taken as part of the background test. Two were Herbicide Orange. The fourth sample was of herbicide-contaminated water that was flashed during the third burn. The waste feed samples were analyzed by the following procedures:

- GC analysis for C6-C17 hydrocarbons
- GC/MS for qualitative analysis

The results of the C7-C16 GC analysis are given in Table 22. It can be seen that the diesel fuel feed had a substantial content of compounds boiling below 300°C. The two herbicide feeds have only small amounts of compounds boiling below 300°C. The fourth feed sample had no detectable amounts of organic compounds boiling below 300°C. (Both 2,4-D and 2,4,5-T, which comprise more than 90% of Herbicide Orange, have boiling points well above 300°C.)

TABLE 22. RESULTS OF C7-C16 GC ANALYSES OF FEEDSTOCKS

Boiling Point Range, °C		Concentration in Sample, mg/ml			
		HO-1-CF-714-F	HO-1-CF-716-H	HO-2-CF-813-H	HO-3-CF-813-H
C7	90-110	<0.7	<0.7	<0.7	<0.7
C8	110-140	<0.7	<0.7	<0.7	<0.7
C9	140-160	<0.7	<0.7	<0.7	<0.7
C10	160-180	<0.7	<0.7	<0.7	<0.7
C11	180-200	200	<0.7	<0.7	<0.7
C12	200-220	<0.7	<0.7	<0.7	<0.7
C13	220-240	<0.7	<0.7	<0.7	<0.7
C14	240-260	<0.7	<0.7	<0.7	<0.7
C15	260-280	<0.7	<0.7	<0.7	<0.7
C16	280-300	180	6.5	11	<0.7
Total		380	6.5	11	<0.7

The results of the GC/MS analyses of the waste feeds are given in Table 23. This analysis was quantitative for 2,4-D and 2,4,5-T to an accuracy of ± factor of 2. Quantitation of other identified compounds is ± factor of 10. Each feed was analyzed after first having been diluted a thousandfold with pentane. The two herbicide feeds were also analyzed neat (i.e., not diluted); both of these samples were identical.

4.2.3.2 Analysis of Lear-Siegler Train Samples

After sample penetration, a 0.5-ml aliquot of each concentrate was evaporated to constant weight to obtain a measure of nonvolatile residue, that is, organic compounds boiling at greater than 300°C. The probe and heat-traced line rinse samples gave high residue weights. It was decided to determine whether these residues were partially inorganic. Small portions of the residues were analyzed by thermogravimetric analysis (TGA). These results are given in Table 24. Because the furnace atmosphere was nitrogen, only organic carbon was determined; nonorganic carbon (e.g., graphite, carbon black) was not determined. The weight loss at 300°C was taken as a measure of volatile organics; the weight loss at 900°C was taken as a measure of the total organic compound content of a sample. The data in Table 24 show that the nonvolatile residues from the probe

TABLE 23. RESULTS OF GCMS ANALYSES OF FEEDSTOCKS

Sample	Compound	Concentration parts per thousand
HO-1-CF-714-F*	Hydrocarbons	Major
	Fluorene (i-pr)	5
HO-1-CR-716-H*	2,4-D	1000 (≅ 50%)
	2,4,5-T	1000 (≅ 50%)
HO-2-CF-813-H*	2,4-D	1000 (≅ 50%)
	2,4,5-T	1000 (≅ 50%)
HO-3-CF-828-H*	Nothing other than solvent	<1
HO-1-CF-716-H†	Trichlorophenol	Trace
	Trichloroanisole	Trace
	Dichloromethoxybenzene	Trace
	Monochlorophenoxyacetic acid, butyl ester	Trace
	2,4-D	Major
	2,4,5-T	Major
	Dichloromethoxyanisole, octyl ester	Trace
	Dichlorodibenzo-p-dioxin	Trace
HO-2-CF-813-H†	Same as neat sample of HO-1-CF-716-H	

*These samples were diluted 1000-fold in pentane. Detection limit was 1 μg/ml.

†These samples were run neat. The detection limit was 50 ng/μl.

TABLE 24. ORGANIC CONTENTS OF LEAR-SIEGLER TRAIN SAMPLES FROM THERMOGRAVIMETRIC ANALYSES

Sample	Percent Loss by 300°C	Percent Loss by 900°C
HO-1-LR-716	34.8	70.0
HO-1-PR-171	41.3	69.3
HO-2-LR-813	70.4	71.5
HO-2-PR-813	24.5	46
HO-3-LR-828	43.6	59.2
HO-3-PR-828	39.8	60.8

and heat-traced line rinses were significantly inorganic. For example, the 70% weight loss from HO-1-LR-716 indicates that the residue was 30% inorganic. Correcting the residue weights for inorganic content gives a better estimation of emissions of organic compounds with boiling points above 300°C.

Table 25 presents the results of the gravimetric analyses of the Lear-Siegler train samples, corrected for solvent blanks and inorganic contents. These corrected weights, corresponding to hydrocarbons with boiling points greater than 300°C, are used in conjunction with infrared spectral analysis to give information about emissions of the classes of nonvolatile hydrocarbons emitted during the incineration.

Each residue was also analyzed by infrared spectrophotometry. Qualitative interpretations of the IR spectra in terms of classes of compounds found in the residues are given in Table 26. Phthalate esters and/or silicones were found in most of the residues. These are ubiquitous compounds and are frequently found as contaminants in trace organic analyses. Precautions were taken in both the sampling and analysis operations in this program, but it seems that contamination occurred and in a random fashion. Because the phthalate esters and silicones are present in unknown quantities, no assessment as to emissions of nonvolatile hydrocarbons can be made. The presence of substituted benzene compounds and polynuclear aromatic hydrocarbon in most of the samples is noteworthy. Analyses to be discussed later will show that these compounds are not waste components, but rather, are probably synthesized in the flame.

TABLE 25. RESULTS OF GRAVIMETRIC ANALYSES OF LEAR-SIEGLER TRAIN SAMPLES*

Sample	Residue Weight mg	Volume Concentrated ml†	Blank Correction mg	Volume of Sample	Organic Fraction %	Weight in Sample mg
HO-1-ST-714-F	0.561	298/300	0.422		‡	1.837
HO-1-LR-714-F	0.250	248/250	0.620	2098	‡	3.256
HO-1-ST-716-H	0.727	348/350	0.422		‡	2.503
HO-1-LR-716-H	184.572	248/250	0.620	2191	70.0	4562
HO-1-PR-717-H	337.873	248/250	0.620	310	69.3	1170
HO-2-ST-813-H	2.195	298/300	0.422		‡	8.417
HO-2-LR-813-H	386.786	248/250	0.620	1031	71.5	4597
HO-2-PR-813-H	218.946	248/250	0.620	398	46.0	646
HO-3-ST-828-H	2.827	198/200	0.422		‡	11.000
HO-3-LR-828-H	216.918	248/250	0.620	1485	59.2	3074
HO-3-PR-828-H	98.089	248/250	0.620	383	60.8	368

*Sample calculation in Appendix F.5.

†This notation indicates that, for example, 298 ml of the 300 ml extract volume of the sorbent trap of 7/14/77 was concentrated.

‡These residues were too small to perform thermogravimetry.

TABLE 26. CLASSES OF NONVOLATILE ORGANIC COMPOUNDS PRESENT IN LEAR-SIEGLER TRAIN SAMPLES

Sample	Compound Classes
HO-1-ST-714-F	Phthalate esters, disubstituted benzene compounds, chlorinated compounds
HO-1-LR-714-F	Phthalate esters, organosilicones
HO-1-ST-716-H	Phthalate esters
HO-1-LR-716-H	Substituted benzene compounds, polynuclear aromatic hydrocarbons, aldehyde-ketone
HO-1-PR-717-H	Substituted benzene compounds, polynuclear aromatic hydrocarbons
HO-2-ST-813-H	Phthalate esters
HO-2-LR-813-H	Silicone compounds
HO-2-PR-813-H	Esters-aldehydes-ketones, benzenoid compounds
HO-3-ST-828-H	Phthalate esters, disubstituted benzene compounds, chlorinated compounds
HO-3-LR-828-H	Esters, benzene derivatives
HO-3-PR-828-H	Silicones

A measure of the volatile organic compound content of the Lear-Siegler train samples was obtained from the C7-C16 GC procedure. Results of these analyses are presented in Table 27 which gives, as emission concentrations, the amounts of material detected in each boiling point range and the total chromatographable organic content. It is seen from the results in Table 27 that the probe and heat-traced lines rinse samples had substantial quantities of chromatographable organic compounds. Although these analyses were performed on neat (unconcentrated) portions of the samples, water and aqueous HCl are not detected and do not contribute to the total chromatographable organic content.

In the Level I organic analysis scheme, if a residue weight, calculated at the source, exceeds a certain concentration (0.5 mg/m^3 and 0.1 mg/kg for liquids and solids), then a suitably sized portion of the extract is taken for liquid chromatographic separation. The separation yields eight fractions, each of which contains reasonably distinct classes of organic compounds. This simplifies the identification of compound classes and gives an estimate of the amounts of compound classes present in the sample. Each fraction is evaporated to constant weight. Nonvolatile residue weight is recorded, and an infrared spectrum is measured on each residue.

TABLE 27. EMISSIONS OF VOLATILE ORGANIC COMPOUNDS FROM C7-C16 GC ANALYSES OF LEAR-SIEGLER TRAIN SAMPLES*

Sample	Emission Concentration, ppm C7 90-120°C	 C8 120-140°C	 C9 140-160°C	 C10 160-180°C	 C11 180-200°C	 C12 200-220°C	 C13 220-240°C	 C14 240-260°C	 C15 260-280°C	 C16 280-300°C	Detection Limit mg/m^3	Total Chromatographable Organic Content mg/m^3
HO-1-ST-714F	+	+	+	0.23	+	+	+	0.15	+	+	<0.05	0.38
HO-1-LR-714F	+	7.5	+	3.7	+	+	+	2.7	+	+	<0.4	14
HO-1-ST-716-H	+	+	+	0.23	+	+	+	0.12	+	+	<0.04	0.35
HO-1-LR-716-H	+	+	+	4.3	+	1.1	2.2	2.9	1.6	+	<0.3	12.1
HO-1-PR-717-H	+	7.6	+	0.1	+	+	+	0.08	+	+	<0.01	7.8
HO-2-ST-813-H	0.61	0.14	+	+	+	+	+	+	0.10	+	<0.02	0.85
HO-2-LR-813-H	+	+	+	2.3	+	0.23	+	+	+	+	<0.08	3
HO-2-PR-813-H	+	+	13	6.0	+	0.50	0.09	0.09	0.27	2.6	<0.03	26
HO-3-ST-828-H	+	+	+	+	+	+	+	+	+	+	<0.02	<0.2
HO-3-LR-828-H	2.2	8.0	+	0.65	+	+	+	+	+	+	<0.2	11
HO-3-PR-828-H	+	3.4	+	+	+	+	+	+	+	+	<0.04	3.4

*Gas volumes corrected to 20°C. Sample calculation in Appendix F.6. See Appendix F.12 for conversion of mg/m^3 to ppm.

+Indicates nothing was detected in that range. The column labeled Detection Limit shows the amount of material which could have been present without being detected. The pluses were used to highlight what was found rather than what was not found, since most of the entries would be less than values. The detection limit for these analyses was 0.7 ng/µ ℓ injected.

Table 28 gives the residue weights of the Lear-Siegler train samples separated by liquid chromatography. While all of the samples except the sorbent traps of 7/14/77 and 7/16/77 met the criterion for the separation, only those samples listed in Table 28 had sufficient material to perform the separation. It is sometimes difficult to dry the latter three fractions, which contain methanol in the eluent. Infrared spectra of several fractions showed that they were not dry or were indistinguishable from the corresponding blank. Two fractions (6 and 7) in the line rinse of 8/13/77 evidently contained inorganic acids, as the aluminum evaporation-weighing dishes were partially dissolved.

Table 29 presents the interpretations of the IR spectra of the residues from the LC separations which had sufficient material (greater than 0.1 mg). Phthalate esters and/or silicones were again found in most of the residues. Benzenoid compounds and polynuclear aromatic hydrocarbons were also found in the line and probe rinse fractions.

Gas chromatographic-mass spectrometric analyses were performed on the concentrates from the Lear-Siegler train samples. These analyses were quantitative for 2,4-D and 2,4,5-T. An attempt was made to identify other compounds found and to give semiquantitative estimates of amounts. The results of these analyses are given in Table 30. There were a number of unidentifiable compounds. The major reason for not being able to identify a compound was the lack of a reference spectrum in the GC/MS spectral data library. To identify a compound, the mass spectrum of that compound is compared with reference mass spectra in the library. If no match is found, the compound cannot be identified.

It is noteworthy that neither 2,4-D nor 2,4,5-T was found in any of the Lear-Siegler train samples. Phthalate esters and/or silicones were found in all of the samples. Many interesting compounds were found. Fluorene was found in the diesel fuel and in the line rinse from the fuel oil background. Dichlorobiphenyl, a polychlorinated biphenyl, was found in the sorbent trap samples taken when herbicide was burned. However, no other polychlorinated biphenyls were identified. The probe and heat-traced line rinses from the herbicide tests contained a variety of aromatic compounds. A number of polynuclear aromatic compounds were identified.

TABLE 28. GRAVIMETRIC RESULTS OF LIQUID CHROMATOGRAPHIC SEPARATIONS OF LEAR-SIEGLER TRAIN SAMPLES

	Sample, Residue Weight in mg						
Fraction	HO-1-LR-716	HO-1-PR-716	HO-2-LR-813	HO-2-PR-813	HO-3-LR-828	HO-3-PR-828	Blank
1	0.0	0.2	0.1	2.9	0.0	4.4	0.0
2	0.0	2.1	0.0	0.0	0.0	0.1	0.0
3	0.1	0.7	0.3	7.2	0.0	0.5	0.0
4	0.0	3.5	0.2	46.3	0.0	0.2	0.0
5	0.1	73.8	0.0	32.5	1.4	6.6	0.5
6	171.4	87.2[‡]	284.1[*]	68.5	136.4	75.0	1.0
7	90.5[‡]	30.5[‡]	184.4[*]	27.4	54.5	36.2	6.5
8	31.1[‡]	11.2[‡]	11.9[‡]	6.8[‡]	12.5[‡]	19.2[‡]	15[†]

[*] These fractions contained acids which reacted with the aluminum weighing pans. The eighth fraction eluent contains HCl, so that these solutions were evaporated in glass dishes.

[†] This sample was lost in analysis. The value reflects past experience with these fractions.

[‡] These fractions were wet and/or had IR spectra indistinguishable from the corresponding blank.

TABLE 29. COMPOUND CLASSES PRESENT IN LC FRACTIONS FROM LEAR-SIEGLER TRAIN SAMPLES*

Sample	Compound Classes
HO-2-LR-813	
Fraction 1	Saturated aliphatic hydrocarbons
Fraction 6	Same as blank
Fraction 7	Same as blank
Fraction 8	Same as blank
HO-3-LR-828	
Fraction 5	Phthalate esters
Fraction 6	Phthalate esters
Fraction 8	Same as blank
HO-3-PR-828	
Fraction 1	Esters; silicones; benzene derivatives, including PAH compounds; aldehydes-ketones
Fraction 3	Esters, silicones, aldehydes-ketones
Fraction 5	Esters, silicones, aldehydes-ketones
Fraction 6	Esters, silicones, aldehydes-ketones
Fraction 7	Same as blank
HO-1-LR-716	
Fraction 3	Phthalate esters
Fraction 6	Esters
Fraction 8	Same as blank

(continued)

* IR spectra were not run on residues with weights less than 0.1 mg.

TABLE 29. (continued)*

Sample	Compound Classes
HO-1-PR-717	
Fraction 2	Phthalate esters
Fraction 3	Phthalate esters
Fraction 4	Esters, aldehydes-ketones, benzene derivatives, silicones
Fraction 5	Esters, aldehydes-ketones, benzene derivatives
Fraction 8	Same as blank
HO-2-PR-813	
Fraction 1	Benzene derivatives, including PAH compounds; esters; aldehydes-ketones
Fraction 2	Benzene derivatives, including PAH compounds; aldehydes-ketones; silicones
Fraction 3	Benzene derivatives, including PAH compounds, esters; aldehydes-ketones; silicones
Fraction 4	Benzene derivatives, esters, aldehydes-ketones
Fraction 5	Esters, aldehydes-ketones
Fraction 6	Esters, aldehydes-ketones
Fraction 7	Aldehydes-ketones
Fraction 8	Same as blank

* IR spectra were not run on residues with weights less than 0.1 mg.

TABLE 30. GC/MS ANALYSES OF LEAR-SIEGLER TRAIN SAMPLES*

Sample	Compound	Concentration ng/μl	Stack Concentration μg/m^3
HO-1-ST-714	Organo-silicone	10	5
	Organo-silicone	10	5
	Phthalate ester	5	3
	Phthalate ester	5	3
HO-1-LR-714	Phthalate ester	5	20
	Fluorene - $(CH_3)_5$	10	40
HO-1-ST-716	Dichlorobiphenyl	10	3
	Phthalate ester	2	0.7
	Unknown, chlorinated	10	3
HO-1-LR-716	Substituted aromatic	5	15
	Organo-silicone	5	15
	$C_{14}H_{22}$, subst. aromatic	5	15
	$C_{14}H_{22}$, subst. aromatic	5	15
	Substituted aromatic	5	15
	Substituted aromatic	5	15
	Substituted aromatic	5	15
	Substituted aromatic	5	15
	Pyrene	5	15
	Organo-silicone	5	15
HO-1-PR-717	Organo-silicone	5	0.8
	Hydrocarbons	Major	

(continued)

*Sample calculation in Appendix F.7. See Appendix F.12 for conversion of μg/m^3 to ppb. The detection limit was 1 ng/μl. Accuracy for 2,4-D and 2,4,5-T was ± factor of 2. Accuracy for other species was ± factor of 10.

TABLE 30. (continued)

Sample	Compound	Concentration ng/µl	Stack Concentration µg/m^3
HO-2-ST-813	Aromatic	100	20
	Dichloroaromatic	100	20
	Trichlorophenol	50	10
	Trichloroaromatic	20	5
	Dichlorobiphenyl	20	5
	Phthalate ester	20	5
	Unknown, chlorinated	50	10
	Benzil	20	5
	Phthalate ester	1000	230
HO-2-LR-813	Organo-silicone	50	50
HO-2-PR-813	Organo-silicone	Major	
	Many other unidentified compounds	Major	
HO-3-ST-828	Unknown, chlorinated	100	30
	Dichlorobiphenyl	10	3
	Chloromethylacenapthene	10	3
	Unknown, chlorinated	100	30
	Benzil	100	30
	Phthalate ester	100	30
HO-3-LR-828	$(CH_3)_x$-aromatic (MW 288)	50	90
	$(CH_3)_x$-aromatic (MW 288)	50	90
	Organo-silicone	10	20
	$(CH_3)_x$-aromatic (MW 202)	10	20

(continued)

TABLE 30. (continued)

Sample	Compound	Concentration ng/μl	Stack Concentration μg/m^3
HO-3-LR-828 (Cont.)	$(CH_3)_x$-aromatic	5	10
	Organo-silicone	10	20
	Pyrene	10	20
	Organo-silicone	5	10
	Phthalate ester	5	10
	$(CH_3)_x$-aromatic (MW 196)	5	10
HO-3-PR-828	Chloro-aromatic (MW 218)	100	50
	Anthracene	100	50
	$(CH_3)_x$-aromatic (MW 200)	100	50
	$(CH_3)_x$-aromatic (MW 216)	10	5
	$(CH_3)_x$-aromatic (MW 276)	10	5
	$(CH_3)_x$-aromatic (MW 216)	10	5
	Methyl, ethyl-pyrene	10	5
	$(CH_3)_x$-aromatic (MW 258)	10	5
	$(CH_3)_x$-aromatic (MW 240)	10	5
	$(CH_3)_x$-aromatic (MW 240)	10	5
	$(CH_3)_x$-pyrene	10	5
	$(CH_3)_x$-aromatic (MW 240)	10	5
	$(CH_3)_x$-aromatic (MW 240)	10	5
	$(CH_3)_x$-aromatic (MW 316)	10	5
	$(CH_3)_x$-aromatic (MW 316)	10	5
	$(CH_3)_x$-aromatic (MW 300)	10	5

(continued)

TABLE 30. (continued)

Sample	Compound	Concentration ng/µl	Stack Concentration µg/m3
HO-3-PR-828 (Cont.)	$(CH_3)_x$-aromatic (MW 296)	10	5
	$(CH_3)_x$-aromatic (MW 298)	10	5
	$(CH_3)_x$-aromatic (MW 280)	10	5
	$(CH_3)_x$-aromatic (MW 298)	10	5
	Phthalate ester	10	5
	$(CH_3)_x$-aromatic (MW 356)	10	5
	$(CH_3)_x$-aromatic (MW 314)	10	5
	$(CH_3)_x$-aromatic (MW 336)	10	5
	$(CH_3)_x$-aromatic (MW 336)	10	5

4.2.3.3 Results of Analyses of Gas Sampling Bags

The XAD-2 resin in the sorbent trap does not efficiently collect organic compounds with boiling points below about 90°C. Therefore, samples of combustion effluent were acquired in Tedlar® gas sampling bags. The contents of the bags were analyzed by the C1-C6 GC procedure. The results are presented in Table 31. Because of inadvertent delays in transportation, the samples must be considered compromised. During the several weeks delay between acquisition and analysis, reactive species are probably lost entirely. Irreversible absorption and condensation also occur in gas sampling bags and probably occurred in these. Hydrocarbons were detected at the 10 to 20 ppm level in every test onboard the M/T Vulcanus, yet only one of the three grab gas samples showed detectable levels of hydrocarbons.

4.2.3.4 Burner Residue Analyses

The nonvolatile residues obtained from the burner residue extracts were large, as were the residues from the probe and heat-traced line extracts. Therefore, thermogravimetric analyses of these residues were also performed. The results of these analyses are given in Table 32. The analyses show that the residues from the burner residue extracts are essentially wholly organic in content.

Table 33 presents the results of the gravimetric analyses of the burner residue extracts. It is seen that the burner residues have contents of extractable nonvolatile organic compounds of from 3.1 to 10.2%. The burner residues are probably mostly inorganic carbon.

TABLE 31. RESULTS OF C1-C6 ANALYSES OF GRAB GAS SAMPLES

Sample	Concentration of C1-C6 Hydrocarbons ppm
HO-1-GG-714	ND*
HO-1-GG-716	+
HO-2-GG-813	22
HO-3-GG-828	ND*

*ND means not detected. Detection limit was 1 ppm.

+Not Acquired

TABLE 32. ORGANIC CONTENTS OF BURNER RESIDUE EXTRACTS FROM THERMOGRAVIMETRIC ANALYSES

Sample	% Loss By 300°C	% Loss By 900°C
HO-1-BR-722	100	100
HO-2-BR-815	97.3	98

TABLE 33. RESULTS OF GRAVIMETRIC ANALYSES OF BURNER RESIDUE SAMPLES

Sample	Residue Weight mg	Volume Concentrated ml	Weight in Sample mg	Organic Fraction %	Weight of Sample g	Concentration mg/g
HO-1-BR-722	64.251	498/500	258.036	100	8.3025	31
HO-2-BR-815	77.714	498/500	312.104	98	3.0017	102

A measure of the volatile organic content of the burner residue extracts is given by the C7-C16 GC analyses. Results of these analyses are given in Table 34. These data show a low volatile organic content.

The residue weights from both burner residue extracts exceeded the criteria for performing in GC separation. Table 35 presents the weights of the residues from the fractions into which these samples were separated. The recovery from one sample was high and probably the result of insufficient drying.

Infrared spectra were taken on the residues from each of the fractions. The interpretation of these spectra in terms of classes of compounds are given in Table 36. Phthalate esters and silicones were again found. However, the herbicide components 2,4-D and 2,4,5-T were found, as well as a phenoxy compound and a carboxylic acid.

GC/MS analyses were performed on the burner residue extracts, and the results are presented in Table 37. The major herbicide components, 2,4-D and 2,4,5-T, were found as were other minor components. In the previous at-sea incineration program,(5) traces of waste feed components were also found in the

TABLE 34. RESULTS OF C7-C16 GC ANALYSES OF BURNER RESIDUE SAMPLES

	Sample, Concentration in mg/g	
Range	HO-1-BR-722	HO-2-BR-815
C7	<0.04	<0.01
C8	<0.04	1.7
C9	<0.04	<0.1
C10	0.3	<0.1
C11	<0.04	<0.1
C12	<0.04	<0.1
C13	<0.04	<0.1
C14	0.18	<0.1
C15	0.60	0.5
C16	0.42	<0.1
Total	1.5	2.2

burner residue samples. The presence of waste feed components in the burner residues implies that the rotating cup burners remain quite cool relative to the flame and the incinerator walls.

4.2.4 Wright State University Analytical Methodology

Wright State University has, under contract to the U.S. Air Force, developed methodology for determining TCDD in Herbicide Orange and in samples relating to the storage and disposal of Herbicide Orange. Details of WSU methodology may be found in Reference 6.

TCDD in composite feeds was isolated from the bulk of feedstock by liquid chromatography on a mixed-bed silica gel/alumina column. The fraction containing TCDD was taken to dryness. Prior to analysis, the residue was taken up in a known volume of benzene.

TABLE 35. GRAVIMETRIC RESULTS OF LC SEPARATIONS OF BURNER RESIDUES

	Sample, Residue Weight in mg		
Fraction	HO-1-BR-722	HO-2-BR-815	Blank
1	60.1	33.0	0.0
2	3.1	32.5	0.0
3	13.2	42.1	0.0
4	5.2	15.5	0.0
5	3.2	0.2	0.5
6	2.8	3.9	1.0
7	4.3‡	20.7‡	6.5
8	17.0‡	19.3‡	15*

*This sample was lost. The value reflects past experience for these fractions.

†Corrected for blanks.

‡These samples were not completely dry, and their infrared spectra were indistinguishable from the corresponding blanks.

A portion of each impinger sample was washed with aqueous base and then water. After washing, the organic fraction was dried over anhydrous sodium sulfate. After drying, the organic layer was decanted and combined with a petroleum ether wash of the sodium sulfate. Both organic layers were taken to dryness. Prior to analysis, the residue was dissolved in a known volume of benzene.

A 10 ml portion of each probe and line rinse was reduced in volume to 0.5 ml and then diluted to 1.0 ml with benzene. The samples then consisted of a brown, water miscible layer and the benzene layer. Aliquots of the benzene layer were taken for analysis.

Analyses for TCDD were performed on an AEI MS-30 double focusing mass spectrometer coupled to a Varian 1440 gas chromatograph.

TABLE 36. COMPOUND CLASSES PRESENT IN LC FRACTIONS FROM BURNER RESIDUE SAMPLES*

Sample	Compound Classes
HO-1-BR-722	
Fraction 1	Substituted aliphatic hydrocarbons
Fraction 2	Hydrocarbons; traces of 2,4-D and 2,4,5-T
Fraction 3	2,4-D; 2,4,5-T
Fraction 4	2,4-D; 2,4,5-T
Fraction 5	Phthalate esters, traces of 2,4-D and 2[illegible],5-T
Fraction 6	Esters; silicones; 2,4-D and 2,4,5-T
Fraction 7	Esters, silicones
HO-2-BR-815	
Fraction 1	2,4-D; 2,4,5-T
Fraction 2	2,4-D; 2,4,5-T
Fraction 3	2,4-D; 2,4,5-T
Fraction 4	2,4-D; 2,4,5-T
Fraction 6	2,4-D; 2,4,5-T
Fraction 7	Aliphatic nitro compound, benzene derivatives, phenoxy compound, carboxylic acid

* IR spectra were not run on residues with weights less than 0.1 mg.

TABLE 37. RESULTS OF GC/MS ANALYSES OF BURNER RESIDUE SAMPLES

Sample	Compound	Concentration mg/g
HO-1-BR-712	2,4-D	0.1
	2,4,5-T	0.12
	Hydrocarbons	Major
	Methoxy-2,4-D	0.005
HO-2-BR-815	2,4-D	0.7
	2,4,5-T	0.7
	Chlorophenoxyacetic acid, butyl ester	0.01
	Methoxy-2,4-D	0.67
	Octyl ester of 2,4-D	0.07
	Octyl ester of 2,4,5-T	0.07

4.2.5 Wright State University Analytical Results

Because of its extensive experience in the analysis of TCDD in Herbicide Orange and related environmental samples, the Brehm Laboratory of Wright State University was selected by the U.S. EPA and the U.S. Air Force to perform analyses of combustion effluent samples for the purpose of determining permit compliance with respect to emissions of TCDD.

Table 38 presents results of the WSU analyses of the combustion effluent samples for TCDD. It is seen that TCDD was detected in only the line and probe rinse samples of 8 August (HO-2-LR-808-4 and HO-2-PR-808-H, respectively). Comparison of the minimum detectable concentrations shows that they vary widely. For example, TCDD was not detected in any of the benzene impinger samples, yet the minimum detectable concentrations ranged from <0.00094 ng/ml (HO-1-BI-716-H) to <0.047 ng/ml (HO-2-BI-813-H). This variation was a consequence of the complexity of the samples. There was (Section 4.2.3) a large number of organic compounds in the samples. Many of these compounds were similar to TCDD in molecular weight; consequently, the state-of-the-art methodology being employed was not capable of completely separating TCDD from these extraneous compounds. These compounds thus acted as interferences in the determination of TCDD and

TABLE 38. RESULTS OF WSU ANALYSES OF STACK SAMPLES FOR TCDD

Sample	TCDD Found*	Minimum Detectable Quantity
HO-1-CF-714-F (feed)	ND	<0.02 μg/mℓ
HO-1-BI-714-F	ND	<0.0015 ng/mℓ
HO-1-LR-714-F	ND	<0.086 ng/mℓ
HO-1-CF-716-H (feed)	2.5 μg/mℓ	<0.02 μg/mℓ
HO-1-BI-716-H	ND	<0.00094 ng/mℓ
HO-1-LR-716-H	ND	<0.045 ng/mℓ
HO-1-PR-717-F	ND	<0.086 ng/mℓ
HO-2-CF-808-H (feed)	2.8 μg/mℓ	<0.02 μg/mℓ
HO-2-BI-808-H	ND	<0.034 ng/mℓ
HO-2-LR-808-H	0.136 ng/mℓ	—
HO-2-PR-808-H	3.34 ng/mℓ	—
HO-2-CF-813-H (feed)	1.0 μg/mℓ	<0.02 μg/mℓ
HO-2-BI-813-H	ND	<0.047 ng/mℓ
HO-2-LR-813-H	ND	<0.11 ng/mℓ
HO-2-PR-813-H	ND	<0.30 ng/mℓ
HO-3-CF-828-H (feed)	2.8 μg/mℓ	<0.02 μg/mℓ
HO-3-BI-828-H	ND	<0.040 ng/mℓ
HO-3-LR-828-H	ND	<0.012 ng/mℓ
HO-3-PR-828-H	ND	<0.048 ng/mℓ

*ND indicates not detected.

caused minimum detectable concentrations to be variable and higher than they would have been in the absence of the interferences.

4.2.6 Battelle-Columbus Laboratories Analytical Methodology

Battelle-Columbus Laboratories (BCL), under contract to the U.S. Air Force, set up and staffed a laboratory on Johnston Island for land based environmental monitoring during the dedrumming operation. BCL provided quick-response analyses for 2,4-D and 2,4,5-T in combustion effluent and drinking water samples from the shipboard incineration. BCL also analyzed for 2,4-D and 2,4,5-T the workspace air monitor Chromosorb 102® samples taken onboard the ship.

Combustion effluent samples (probe and heat-traced lines rinses and benzene impingers) were analyzed directly by gas chromatography with electron capture detection (GC-ECD). Ship's drinking water samples were first extracted with hexane and then analyzed by GC-ECD. The Chromosorb 102® tube workspace air monitor samples were extracted in a soxhlet apparatus for 1 hour with pentane, concentrated, and then analyzed by GC-ECD.

4.2.7 Battelle-Columbus Laboratories Analytical Results

4.2.7.1 Analyses of Workspace Air Monitor Samples

Results of the analyses of workspace air monitor samples by BCL are given in Tables 39 and 40. These results are discussed in Section 5.3.2.

4.2.7.2 Analyses of Combustion Effluent Samples

Table 41 presents the results of analyses of combustion effluent samples by BCL. A peak having the correct retention time for 2,4-D was found in the chromatogram of the probe rinse of 8/13/77. This cannot, however, be considered conclusive proof that 2,4-D was present. Neither 2,4-D nor 2,4,5-T were found in any other combustion effluent sample.

4.2.7.3 Analyses of Potable Water Samples

Three samples of drinking water from the M/T Vulcanus were analyzed for 2,4-D and 2,4,5-T. Neither compound was detected, as shown in Table 42.

TABLE 39. RESULTS OF BCL ANALYSES OF FIRST BURN WORKSPACE AIR MONITORS*

Date of Sample 1977		Combustor Room, ~93°C			Pump Room, ~32°C			Dining Room, ~24°C			Sea Container, ~23°C		
		2,4-D µg/m³*	2,4,5-T µg/m³	Total µg/m³	2,4-D µg/m³	2,4,5-T µg/m³	Total µg/m³	2,4-D µg/m³	2,4,5-T µg/m³	Total µg/m³	2,4-D µg/m³	2,4,5-T µg/m³	Total µg/m³
13 July	Night	✦	✦	✦	0.42	0.1	0.52	✦	✦	✦	✦	✦	✦
14 July	Day	<0.22	0.06	<0.28	✦	✦	✦	✦	✦	✦	✦	✦	✦
14 July	Night	✦	✦	✦	✦	✦	✦	✦	✦	✦	✦	✦	✦
15 July	Day	✦	✦	✦	✦	✦	✦	<0.22	<0.08	<0.31	≤0.58	≤0.29	≤0.87
15 July	Night	✦	✦	✦	1.43	0.55	1.98	✦	✦	✦	✦	✦	✦
16 July	Day	✦	✦	✦	62.2	10.8	73	0.26	≤0.29	≤0.55	≤0.58	≤0.29	≤0.88
16 July	Night	<0.76	<0.38	<1.1	0.99	0.23	1.22	≤1.03	<0.10	≤1.14	≤0.52	<0.08	≤0.59
17 July	Day	✦	✦	✦	3.45	1.26	4.70	✦	✦	✦	✦	✦	✦
17 July	Night	✦	✦	✦	✦	✦	✦	✦	✦	✦	✦	✦	✦
18 July	Day	0.54	≤1.1	≤1.6	✦	✦	✦	≤0.68	<0.10	≤0.78	0.16	≤0.27	≤0.44
18 July	Night	✦	✦	✦	✦	✦	✦	≤0.93	<0.14	≤1.07	0.31	≤0.28	≤0.59
19 July	Day	✦	✦	✦	4.72	2.23	6.96	✦	✦	✦	✦	✦	✦
19 July	Night	✦	✦	✦	✦	✦	✦	✦	✦	✦	✦	✦	✦
20 July	Day	✦	✦	✦	✦	✦	✦	✦	✦	✦	≤0.57	≤0.28	≤0.85
20 July	Night	3.2	1.5	4.7	✦	✦	✦	≤0.53	<0.08	≤0.61	✦	✦	✦
21 July	Day	✦	✦	✦	1.68	0.52	2.20	✦	✦	✦	✦	✦	✦
21 July	Night	✦	✦	✦	✦	✦	✦	✦	✦	✦	✦	✦	✦
22 July	Day	5.1	2.5	7.5	✦	✦	✦	≤0.23	<0.09	<0.31	✦	✦	✦
22 July	Night	✦	✦	✦	✦	✦	✦	✦	✦	✦	≤0.57	<0.08	≤0.66
23 July	Day	✦	✦	✦	✦	✦	✦	✦	✦	✦	✦	✦	✦
23 July	Night	✦	✦	✦	3.00	1.02	4.03	✦	✦	✦	✦	✦	✦
24 July	Day	✦	✦	✦	✦	✦	✦	✦	✦	✦	✦	✦	✦
24 July	Night	0.27	0.16	0.44	✦	✦	✦	✦	✦	✦	✦	✦	✦

*Concentrations are in µg/m³ air sampled at the temperatures given for each location at ambient pressure. The 8-hour TLV for 2,4-D + 2,4,5-T is 10 mg/m³. See Appendix F.12 for conversion to ppm.

✦These samples have been archived.

<Indicates not detected. The numerical value is the detection limit.

≤Indicates present at detection limits.

TABLE 40. RESULTS OF BCL ANALYSES OF SECOND AND THIRD BURN WORKSPACE AIR MONITORS*

Date of Sample 1977	Combustor Room ~93°C			Pump Room ~32°C			Dining Room ~24°C			Sea Container ~23°C		
	2,4-D μg/m³*	2,4,5-T μg/m³	Total μg/m³	2,4-D μg/m³	2,4,5-T μg/m³	Total μg/m³	2,4-D μg/m³	2,4,5-T μg/m³	Total μg/m³	2,4-D μg/m³	2,4,5-T μg/m³	Total μg/m³
7 August	39.7	21.8	61.5	21.1	10.3	31.4	0.56	0.15	0.71	-	-	-
3 August	-	-	-	18.0	5.40	23.4	-	-	-	≤0.28	≤0.14	≤0.42
9 August	3.1	1.59	4.66	-	-	-	1.37	0.48	1.86	-	-	-
10 August	-	-	-	7.31	2.27	9.58	-	-	-	≤0.28	≤0.14	≤0.42
11 August	33.1	18.5	51.6	-	-	-	0.70	0.20	0.90	-	-	-
12 August	-	-	-	15.9	4.84	20.7	-	-	-	≤0.29	≤0.15	≤0.44
13 August	68.3	38.2	107	-	-	-	-	-	-	-	-	-
14 August	-	-	-	0.70	0.22	0.92	-	-	-	-	-	-
15 August	1.73	0.84	2.57	-	-	-	-	-	-	-	-	-
24 August	-	-	-	+	+	+	-	-	-	+	+	+
25 August	47.4	22.7	70.1	+	+	+	0.58	≤0.14	≤0.72	+	+	+
26 August				+	+	+	0.53	≤0.14	≤0.67	+	+	+
27 August	76.4	35.4	112	+	+	+	0.68	0.15	0.83	+	+	+
28 August				+	+	+	-	-	-	+	+	+
29 August	9.97	6.09	16.1	+	+	+	1.52	0.43	1.95	+	+	+
30 August				+	+	+	1.17	0.28	1.45	+	+	+
31 August	114	59.6	174	+	+	+	1.52	0.42	1.93	+	+	+
1 September	-	-	-	+	+	+	1.24	0.32	1.56	+	+	+
2 September	77.6	41.3	119	+	+	+	-	-	-	+	+	+

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*Concentrations are in μg/m³ air sampled at the temperatures given for each location at ambient pressure. The 8-hour TLV for 2,4-D + 2,4,5-T is 10 mg/m³. See Appendix F.12 for conversion to ppm.

-These samples have been archived.

≤Indicates present at detection limits.

+These locations were not monitored during the third burn.

TABLE 41. RESULTS OF BCL ANALYSES OF COMBUSTION EFFLUENT SAMPLES

Sample	2,4-D µg/mℓ	2,4,5-T µg/mℓ
HO-1-BI-714-F	<0.08*	<0.04
HO-1-LR-714-F	<0.02	<0.01
HO-1-BI-715-H	<0.08	<0.04
HO-1-LR-715-H	<0.02	<0.01
HO-1-BI-716-H	<0.08	<0.04
HO-1-LR-716-H	<0.02	<0.01
HO-1-PR-717-H	+	+
HO-1-BI-718-H	<0.08	<0.04
HO-1-LR-718-H	<0.02	<0.01
HO-1-BI-719-H	<0.08	<0.04
HO-1-LR-719-H	<0.02	<0.01
HO-1-PR-722-H	<0.06	<0.03
HO-1-BI-723-H	<0.08	<0.04
HO-1-LR-723-H	<0.02	<0.01
HO-1-PR-725-H	<0.06	<0.03
HO-2-BI-813-H	<0.08	<0.04
HO-2-LR-813-H	<0.02	<0.01
HO-2-PR-813-H	≤0.1	<0.03
HO-3-BI-828-H	<0.08	<0.04
HO-3-LR-828-H	<0.02	<0.01
HO-3-PR-828-H	<0.04	<0.02

*The "<" character indicates not detected. The numerical value is the detection limit.

+This sample was not analyzed.

TABLE 42. RESULTS OF BCL ANALYSES OF SHIP'S DRINKING WATER FOR 2,4-D AND 2,4,5-T

Sample	2,4-D	2,4,5-T
HO-1-SW-724	ND*	ND
HO-2-SW-816	ND	ND
HO-3-SW-828	ND	ND

*ND means not detected. Detection limit was 0.1 ppb (0.1 μg/ℓ).

4.2.8 Marine Monitoring Results

The biological samples were sorted under a microscope, where necessary, to the species level. Identification of some of the species found was difficult because of the paucity of historical collection leading to verified identification of the marine biota in this type of tropical oceanic environment. Nevertheless, it was possible to identify all but a few of the species present. There were slight differences in the species composition among all of the samples, but there was no consistent difference between pre-burn and post-burn tows. It should be noted that the results on copepods from these samples are not essentially different from those obtained on copepods by the USFS Albatross in the period 1887-1909, which are the only other data available on this area of the Pacific.

4.2.9 Onboard Analyses

Instrumentation for onboard analysis consisted of two Shimadzu GC-6AMPFE(s) gas chromatographs, a Shimadzu E1A data processor, and a Shimadzu R-11 recorder. Each GC was a modular unit, equipped with dual flame ionization (FI) detectors, a single electron capture (EC) detector, and a linear temperature programmer. The data processor was microprocessor-controlled and user programmed. The columns were 2 m x 6 mm OD x 2.9 mm ID glass. Three types of columns were available: 3% OV-101, 3% OV-17, and 3% OV-225, respectively, on 80/100 mesh Chromosorb WHP®. The OV-101 column was used exclusively. The injection ports and detector lines had glass inserts. One unit was used as the primary analysis instrument; the other unit was held in reserve.

In order to provide power as free as possible from noise transients, the GC, recorder, and data processor were run off a Shimadzu-supplied transformer to step down the 120V, 60 Hz motor generator power to 100V, 60 Hz.

All onboard analyses were performed isothermally at 170°C. The carrier gas was nitrogen at 30 ml/min. Electron capture was the means of detection. Under these conditions, an analysis required 20 minutes.

4.2.9.1 Analyses of Wipe Samples

Wipe samples were taken daily throughout incineration operations to monitor and determine the effectiveness of the boundary exclusion method of controlling Herbicide Orange contamination. These samples were taken by gently rubbing an approximately 1 m^2 area of surface, e.g., deck, wall, floor, with a Whatman 41® filter paper disc. The discs were extracted by soaking in 5 ml of benzene for 30 minutes, and the extracts were then analyzed using the onboard GC. Because of space and time limitations, wipes could not be extracted exhaustively, as in a soxhlet extractor. Therefore, the efficiency of extraction of 2,4-D and 2,4,5-T from the wipes was not known.

Standards of 2,4-D and 2,4,5-T were obtained from the U.S. EPA. A sample of waste was also used to prepare a standard. There were four major peaks in the U.S. EPA-derived working standards; the waste-derived standard contained corresponding peaks. The presence of all four peaks was required to confirm the presence of 2,4-D and 2,4,5-T in a wipe sample. Because of the unknown extraction efficiency, results of the wipe sample analyses are given as positive (herbicide present) or negative (herbicide absent).

Wipe samples were taken in Gulfport, MI, before and after herbicide was loaded. These wipes served as a background to permit the analysts to distinguish the contribution of previous wastes and ship's lubricants to the chromatograms from 2,4-D and 2,4,5-T. Results of the background wipe samples are given in Table 43. All of the pre- and post-loading wipe samples were negative for 2,4-D and 2,4,5-T.

TABLE 43. SUMMARY OF PRE- AND POST-LOADING WIPE SAMPLES

Location	Pre-Loading	Post-Loading
1. Galley Floor	Neg	-
2. SBD, Entry to Galley	-	Neg
3. SBD, Inside Entry	-	-
4. SBD, Outside Entry	-	Neg
5. SBD, Entry Comb. Rm	Neg	-
6. Bollard(s), Fantail	-	-
7. Top of Fantail Stairs	-	-
8. Comb. Rm, Various	Neg	-
9. Shower, Comb. Rm	-	-
10. PT, Entry Comb. Rm	-	-
11. Outside, Dining Rm	-	-
12. Inside Dining Rm	-	-
13. Dining Rm Floor	-	-
14. PT, Outside Entry	-	-
15. PT, Inside Entry	Neg	-
16. Pump Room Hatch	Neg	-
17. PT, Inside, Entry Pass	-	-
18. PT, Outside Entry Pass	-	Neg
19. Butterworth Hatches	-	-
20. Main Deck, Various	Neg,Neg	Neg
21. Top, 2nd Floor Stairs	Neg	-
22 Foot, Stairs to Bridge	-	-
23. TRW Crew Qtrs	-	-
24. PT, Qtrs Door	-	-
25. PT, Passage, Various	-	-
26. PT, Boat Deck	Neg	-
27. Laundry	Neg	-

- Indicates wipe sample not taken.

Results of wipe sample analyses for the first, second, and third burns are given in Tables 44, 45, and 46, respectively. Figure 17 shows locations where wipe samples were taken. Results are discussed in Section 5.3.1.

4.2.9.2 Analyses of Combustion Effluent Benzene Impinger Samples

After each test, the TRW benzene impinger was analyzed onboard the M/T Vulcanus for 2,4-D and 2,4,5-T. Neither 2,4-D nor 2,4,5-T was detected in any of the benzene impinger samples. Results of these analyses were reported immediately by radio to Johnston Island for transmission to U.S. EPA.

4.2.9.3 Analyses of Air Samples

Samples of workspace air were taken by 10-ml gas sampling syringes for analysis of 2,4-D and 2,4,5-T. None of the air samples showed the presence of these compounds.

4.3 DISCUSSION OF ON-LINE INSTRUMENTATION

4.3.1 Applicability to Compliance Determination

The on-line instrumentation package installed on the M/T Vulcanus for this effort was originally assembled and used for the same purpose during a series of six land-based incinerator test programs to destroy 12 industrial wastes.(4) In addition, essentially the same instrumentation was used on the M/T Vulcanus during at-sea incineration of organochlorine waste in the Gulf of Mexico under Special Permit No. 750D008E.(5) In each test program, incinerator effluent gases were monitored by on-line instrumentation for concentrations of CO_2, CO, hydrocarbons, and O_2.

The concentration of CO in combustion effluent gas is of particular importance because it is a good indicator of the efficiency of the combustion process. Combustion efficiency values are readily calculated from CO_2 and CO measurements. This approach to compliance determination has several advantages. It is real-time, continuous, rapid, and calculations are readily performed. Most importantly, using on-line instrumentation makes compliance determination waste-independent. Therefore, sampling and analysis plans do not have to be designed for each type of waste burned. Further, one need not know waste feed rates to an incinerator to be able to calculate combustion efficiency. For example, if one were measuring chlorinated compounds in the effluent from

TABLE 44. SUMMARY OF FIRST BURN WIPE SAMPLES

	Date								
Location	16 July	17 July	18 July	19 July	20 July	21 July	22 July	23 July	24 July
1. Galley Floor	-	-	-	-	-	-	-	-	Neg, Neg
2. SBD, Entry to Galley	-	Neg	-	-	-	-	-	Pos, Neg	-
3. SBD, Inside Entry	-	-	-	-	-	-	-	-	-
4. SBD, Outside Entry	-	-	-	-	-	-	-	-	-
5. SBD, Entry Comb. Rm	-	-	-	-	-	-	-	-	-
6. Bollard(s), Fantail	-	-	-	-	-	-	-	-	-
7. Top of Fantail Stairs	Neg	Neg	-	-	-	-	-	Neg	-
8. Comb. Rm, Various	-	-	-	Neg	Neg	Neg	-	Pos	-
9. Shower, Comb. Rm	-	-	Neg	-	-	-	-	-	-
10. PT, Entry Comb. Rm	-	Neg	-	Neg	-	-	Neg	Neg	-
11. Outside, Dining Rm	-	-	-	-	-	-	-	-	-
12. Inside Dining Rm	-	-	-	-	-	-	-	-	-
13. Dining Rm Floor	-	-		Neg	-	-	Neg, Neg	-	-
14. PT, Outside Entry	-	-	-	-	-	-	-	-	-
15. PT, Inside Entry	-	-	-	-	-	-	-	-	-
16. Pump Room Hatch	-	-	-	-	-	-	Pos	Pos	-
17. PT, Inside, Entry Pass	-	-	-	-	-	-	-	-	-
18. PT, Outside, Entry Pass	-	-	-	-	-	-	-	-	-
19. Butterworth Hatches	-	-	-	-	-	-	Neg	-	-
20. Main Deck, Various	-	-	-	-	Neg	-	-	-	-
21. Top, 2nd Floor Stairs	-	-	-	-	-	-	-	-	-
22. Foot, Stairs to Bridge	-	-	-	-	-	-	-	-	-
23. TRW Crew Qtrs	-	-	-	-	Pos, Neg	-	-	-	-
24. PT, Qtrs Door	-	Neg	-	-	Neg	-	-	-	-
25. PT, Passage, Various	-	-	-	-	Neg, Neg	-	-	-	-
26. PT, Boat Deck	-	-	-	-	Neg, Neg	Neg	-	-	-
27. Laundry	-	-	-	-	-	-	-	Neg	-

- Indicates wipe sample not taken.

TABLE 45. SUMMARY OF SECOND BURN WIPE SAMPLES

	Date												
Location	7 Aug	7 Aug	8 Aug	9 Aug	9 Aug	10 Aug	11 Aug	12 Aug	13 Aug	13 Aug	14 Aug	15 Aug	16 Aug
1. Galley Floor	-	-	-	-	-	Neg	-	-	-	-	-	-	-
2. SBD, Entry to Galley	-	-	-	-	-	-	-	-	Pos	-	-	Pos	Neg
3. SBD, Inside Entry	-	-	-	-	-	-	-	-	-	-	-	-	Neg
4. SBD, Outside Entry	Pos	Pos	Pos	Pos	-	Neg	Neg	Neg	Neg	-	-	Neg	-
5. SBD, Entry Comb Rm	-	-	-	Neg	Neg (inside)	-	Neg	-	Neg	Neg	Neg	-	Neg
6. Bollard(s), Fantail	-	-	-	-	-	-	-	-	-	-	-	-	-
7. Top of Fantail Stairs	-	-	Neg	-	-	-	-	-	-	-	-	-	
8. Comb Room Various	-	-	-	-	Pos	-	-	-	-	-	-	-	-
9. Shower-Comb Rm	-	-	-	-	Neg	-	-	-	-	-	-	-	-
10. PT, Entry Comb Rm	Pos	-	Neg	Pos	-	Neg	-	Pos	Neg	Neg	Neg	Pos	Neg
11. Outside Dining Rm	Pos	-	Pos	-	-	-	Neg	-	-	-	-	-	-
12. Inside Dining Entry	Pos	-	Pos	-	-	-	-	-	-	-	-	-	-
13. Dining Rm Floor	-	-	-	Pos	-	Neg	Neg	Neg	Neg	-	Neg	Neg	-
14. PT, Outside Entry	Pos	Pos	Pos	Pos	-	Neg	Neg	Neg	Pos	-	-	-	-
15. PT, Inside Entry	-	-	-	-	-	-	-	-	-	-	-	-	-
16. Pump Rm Hatch	-	-	Pos	-	-	-	-	-	-	-	-	-	-
17. PT, Inside Entry Pass.	-	-	-	-	-	-	-	-	-	-	-	-	-
18. PT, Outside Entry Pass.	-	-	-	-	-	-	-	-	-	-	-	-	-
19. Butterworth Hatches	-	-	Pos	-	-	-	-	-	-	-	-	-	-
20. Main Deck, Various	-	-	-	-	-	-	-	-	-	-	-	-	-
21. Top, 2nd Floor Stairs	-	-	-	-	-	-	-	-	-	-	-	-	-
22. Foot, Stairs to Bridge	-	-	-	-	-	-	-	-	-	-	-	-	-
23. TRW Crew Qtrs	-	-	-	-	-	-	-	-	-	-	-	-	-
24. PT, Qtrs Door	-	-	-	-	-	-	-	-	-	-	-	-	-
25. PT Passage, Various	-	-	-	-	-	-	-	-	-	-	-	-	-
26. PT, Boat Deck	-	-	-	-	-	-	-	-	-	-	-	-	-
27. Laundry	-	-	-	-	-	-	-	-	-	-	-	-	-

- Indicates wipe sample not taken.

TABLE 46. SUMMARY OF THIRD BURN WIPE SAMPLES

Location	Date 25 Aug	26 Aug	27 Aug	28 Aug	29 Aug	30 Aug	31 Aug	1 Sep	2 Sep
1. Galley Floor	-	Neg	-	-	-	-	-	-	Pos
2. SBD, Entry to Galley	-	-	-	-	-	-	Pos	Pos	-
3. SBD, Inside Entry	Neg	Neg	Neg	-	Neg	Neg	Neg	Neg	-
4. SBD, Outside Entry	-	-	-	-	-	-	-	-	-
5. SBD, Entry Comb Rm	-	-	-	-	-	-	-	-	-
6. Bollard(s) Fantail	-	-	-	-	-	-	Pos	-	-
7. Top of Fantail Stairs	-	-	-	-	-	-	Neg	-	-
8. Comb Rm, Various	-	-	-	-	-	-	-	-	-
9. Shower, Comb Rm	-	-	-	-	-	-	-	-	-
10. PT, Entry Comb Rm	Neg	Neg	-	-	Pos	Pos	-	Pos	Pos
11. Outside Dining Rm	-	-	-	-	-	-	-	-	-
12. Inside Dining Rm	-	-	-	-	-	-	-	-	-
13. Dining Rm Floor	Neg	Neg	Neg	-	Pos	Pos	Pos	Pos	Pos
14. PT, Outside, Entry	-	-	-	-	-	-	-	-	-
15. PT, Inside, Entry	Pos	Neg	Neg	-	Pos	Pos	Neg	Pos	-
16. Pump Rm Hatch	Pos	-	-	-	-	-	-	-	-
17. PT, Inside Entry Pass	-	-	-	-	-	-	-	-	Pos
18. PT, Outside Entry Pass	-	-	-	-	-	-	-	-	Pos
19. Butterworth Hatches	-	-	-	-	-	-	-	-	-
20. Deck, Main	-	-	-	-	Pos	-	-	-	-
21. Top Qtrs Stairs, 2nd Floor	-	Neg	-	-	-	Pos	-	-	-
22. Foot, Stairs to Bridge	-	-	-	-	-	-	Neg	-	-
23. TRW Crew Qtrs	-	-	-	-	-	-	-	-	-
24. PT, Qtrs Door	-	-	-	-	-	-	-	-	-
25. PT Passage, Various	-	-	-	-	-	-	-	-	-
26. PT, Boat Deck	-	-	-	-	-	-	-	-	-
27. Laundry	-	-	-	-	-	-	-	-	-

- Indicates wipe sample not taken.

1. Galley Floor
2. Sbd. entry to galley
3. Inside Sbd. entry to Qtrs.
4. Outside Sbd. entry to Qtrs.
5. Sbd. entry to Combustion Room
6. Bollard, fantail and Combustion Room
7. Top of fantail stairs
8. Combustion Room, various
9. Shower, Inside
10. Port entry to Combustion Room
11. Entry to dining area
12. Inside dining area
13. Dining Room Floor
14. Outside Port entry to Qtrs.
15. Inside Port entry to Qtrs.
16. Pump Room Hatch
17. Inside Port Passageway entry
18. Outside Port Passageway entry
19. Butterworth Hatches, various
20. Main deck, various
21. Top, 2nd. deck stairs (not shown)
22. Foot of stairs to bridge (not shown)
23. TRW crew Qtrs. (not shown)
24. Port door, Qtrs. (not shown)
25. Port Passage, various (not shown)
26. Port Boat Deck (not shown)
27. Laundry (not shown)

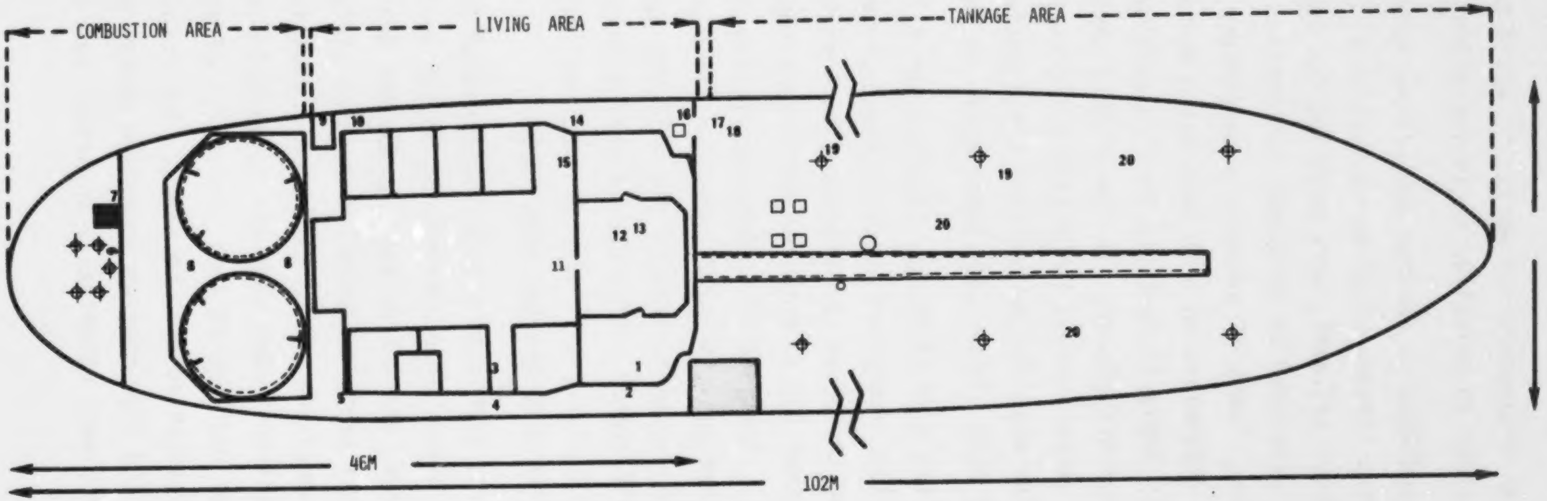
COMBUSTION AREA
LIVING AREA
TANKAGE AREA
7
6
8
8
5
9
10
3
4
14
15
11
12
13
1
2
16
17
18
19
19
20
20
20
20
46M
102M

Figure 17. Location of wipe samples on M/T Vulcanus — summary of three burns.

burning an organochlorine waste, it would be necessary to know the waste feed rate in order to calculate an incineration destruction efficiency.

In addition to on-line monitoring during these test programs, samples of all process streams, such as combustion effluent, incinerator ash, feed stocks, and scrubber effluent, were acquired for laboratory analysis. Results of these analyses were used to calculate destruction efficiencies for specific waste components. Table 47 presents a comparison of combustion and destruction efficiencies determined on both land based and at-sea incineration tests. The results in Table 47 indicate that combustion efficiency compared well with waste destruction efficiency. In those cases where a destruction efficiency was lower than the corresponding combustion efficiency, waste constituents were found in incinerator ash, and destruction efficiencies based on combustion effluent analyses only were higher than those given in the table.

For the Gulf of Mexico tests on the M/T Vulcanus,(5) a special moveable, water-cooled, stainless steel jacketed probe with a quartz liner was developed. This probe traversed the starboard incinerator stack and conducted the combustion effluent gas to both the SASS stack sampling train and the on-line instrumentation. Analysis of on-line monitoring data led to the important conclusion that a fixed-position probe drawing sample gas from a single point in the stack would have served to measure the effluent gas composition and incinerator combustion efficiency. At probe insertion depths greater than 15 cm past the inner wall of the stack, wall effects were negligible, and all calculated combustion efficiencies were greater than 99.9%.

For the Herbicide Orange incineration tests, a fixed-position alumina probe was placed approximately 38 cm (15 in.) past the inner wall of each incinerator stack, and the moveable probe was again placed in the starboard stack. The moveable probe conducted combustion effluent to the sampling trains, while the fixed-position probes conducted combustion effluent gas samples to the on-line monitors. One test was performed with the moveable probe connected to the on-line monitors so that combustion efficiency could be measured as a function of distance across the stack. The results of this test are given in Figure 15 and show that at insertion depths greater than 10 cm combustion efficiencies were essentially invariant and exceeded 99.991%.

TABLE 47. COMPARISON OF COMBUSTION AND DESTRUCTION EFFICIENCIES*

Site	Waste	Combustion Efficiency, %	Destruction Efficiency as Organics,‡ %	Destruction Efficiency, Waste Constituents, %
Rollins Environmental Services	PCBs, hammermilled capacitors	99.99	99.96	>99.999
	PCBs, whole capacitors	99.99	99.94	99.5†
	Nitrochlorobenzene waste	99.99	99.84-99.87	>99.999
3M Company	Polyvinylchloride waste	99.97-99.99	99.80-99.88	99.999
Systech	Phenol waste	99.98-99.99	99.93-99.95	99.99, >99.999
	Monomethylmethacrylate waste	99.98-99.99	99.96-99.98	>99.999
Marquardt	Ethylene waste	99.98	99.86-99.95	>99.999
	Hexachlorocyclopentadiene waste	99.98	99.94-99.95	>99.999
M/T Vulcanus	Organochlorine waste	99.96-99.98	99.91-99.96	99.92-99.98
M/T Vulcanus	Herbicide Orange	99.99	>99.999	>99.99

*Adapted from data in References 4 and 5.

†Overall destruction efficiency reduced by high PCB content in ash. Efficiency based on combustion effluent sampling was >99.999%.

‡This destruction efficiency was based on emissions of all organic compounds.

4.3.2 Problems with On-Line Instrumentation

During land-based incinerator tests, the on-line instrumentation was housed in an automotive van equipped as a portable laboratory. No problems were encountered with the on-line instruments during the land based tests despite the long drives from site to site and corrosiveness of many of the wastes.

For the at-sea incineration tests, a standard shipping container was modified as a portable laboratory to house the instruments. During the Gulf of Mexico tests, a progressive baseline drift of the CO_2 analyzer was encountered, and more frequent calibration was necessary.

During the Herbicide Orange burns, there were considerable difficulties with the on-line instrumentation as described in Section 3.2. Usable data were acquired although more frequent calibration and tuning were necessary. It is believed, however, that problems with the on-line instruments were caused by system design oversights rather than by any problems inherent in the instruments themselves or by their use.

The system design errors were cold spots in the lines conducting the combustion effluent gas samples from the probe to the on-line instruments. A single heat-traced line led from the observation deck to the portable laboratory where it was connected to a manifold. Valves in this manifold permitted the operator to switch the combustion effluent to either gas conditioner. Heat traced lines led from the manifold to the gas conditioner. The manifold itself, however, was not heated. Consequently, condensation may have occurred, and the condensate would have been quite corrosive because of the HCl content of the combustion effluent. The Perma-Pure® dryer in each gas conditioner was designed to remove only water vapor. Therefore, liquid water could have passed through the gas conditioners.

In the equipment mounting rack containing the on-line instruments were inlet and outlet manifolds which distributed sample gas to and recombined sample gas from the instruments. Neither of these manifolds was heated. Condensate was observed in the outlet manifold, and some condensate drained into and damaged the CO analyzers.

Several changes in the design of the on-line monitoring system used in the Herbicide Orange tests would allow extended operation without excessive maintenance, calibration, and tuning:

- Elimination of cold spots in the lines carrying combustion effluent and siting of manifolds so that condensate which might form cannot drain into instruments.
- Addition of condensate traps in lines carrying sample gas. The volumes of these traps should be small so as to minimize instrument response time to concentration changes in the sample gas.
- Substitution of a gas conditioner operating on a different principle, such as refrigeration, for the diffusion-type gas conditioner used thus far. Alternatively, appropriate absorption systems for H_2O and HCl might be found, and gas conditioners could be eliminated.

The extensive test program discussed in this section has demonstrated the feasibility of using on-line monitoring instruments to measure CO_2 and CO concentrations in incinerator effluent streams and to determine permit compliance. The instrumentation package withstood hard travel and corrosive combustion gases. The only problems occurred because of design oversights.

5. SAFETY AND PERSONNEL PROTECTION

This section describes the procedures which were used to protect personnel from exposure to Herbicide Orange and TCDD or their combustion products during the at-sea incineration of the herbicide onboard the M/T Vulcanus. The personnel protection plan was incorporated into the Safety Plan (Appendix A) and thus became part of the permit conditions for the incineration.

Herbicide Orange is an organic chloride consisting of a 50/50 mixture (approximately) of 2,4-D and 2,4,5-T. When drummed, this material contained TCDD as a toxic but minor constituent at levels of 0.5 to 47.0 ppm with an average concentration of 1.9 ppm.(2)

Herbicide Orange (i.e., 2,4-D and 2,4,5-T) has been shown to be moderately toxic and is rapidly eliminated from the body by the kidneys. The American Conference of Governmental Industrial Hygienists (ACGIH) has recommended Threshold Limit Values (TLVs) in air for either 2,4-D or 2,4,5-T to be 10 mg/m^3. The TLV is a time-weighted safe air concentration for an 8-hour day or 40-hour work week. Based on the TLV, a range of time-limited ambient (personnel breathing zone) concentrations considered safe exposure levels for personnel onboard the M/T Vulcanus were set (Appendix A) as follows:

Combined Concentration of Butyl Esters of 2,4-D and 2,4,5-T

2.0 mg/m^3 for samples taken periodically over 16 hours or

10.0 mg/m^3 for samples taken periodically over 8 hours

TCDD has been shown to be extremely toxic, with no-effect dose levels for embryotoxicity and chick edema as low as 0.03 to 0.1 μg/kg/of body weight/day, respectively. The safe ambient concentration for TCDD onboard the M/T Vulcanus was established as 6 ng/m^3 (Appendix A). Furthermore, TCDD in its physiological action is embryotoxic, teratogenic (especially in the first trimester) and acnegenic. It is this extremely high toxicity, with the possibility of organic damage and the disfiguring effects of chloracne, which dictated the type of precautions which were instituted for the protection of personnel involved in the at-sea incineration. The physiological activity and toxicological properties of 2,4-D, 2,4,5-T, and TCDD are discussed in detail in Appendix B.

The methods of entry into the body of both Herbicide Orange and TCDD are by ingestion, absorption through the skin, and inhalation.

5.1 DESIGN OF THE PERSONNEL PROTECTION PLAN

From an operational standpoint, the M/T Vulcanus, pictured in Figure 2 and shown schematically in Figure 17, consists of several functionally discrete parts, each devoted to a specific operation, such as waste storage, propulsion, combustion, and living quarters. Herbicide Orange was handled in the storage and combustion areas.

The living quarters, mess hall, galley, and recreation areas are located between the tankage area (forward) and the combustion room (aft). The location of the various functional portions of the ship are shown in Figure 17. The crew of 18 and the test and observation team of 8 were allowed to move freely about the ship in performing their duties, and to return to the living area for meals, sleep, and recreation. This situation could have resulted in bringing toxic materials into the living quarters unless specific preventive procedures were established.

A personnel protection plan was, therefore, designed to isolate the toxic material in the storage and combustion areas, protect personnel from possible contamination, and prevent the spread of Herbicide Orange into other portions of the ship. Important considerations in the selection of this personnel protection plan were the:

- Confined nature of a shipboard operation
- Centralization of living quarters
- Percutaneous, ingestion, and inhalation paths of exposure
- High toxicity of TCDD.

It was considered mandatory that working personnel be free of contamination before returning to eating and living facilities in order to avoid exposure of others not normally required to come in contact with the chemicals and to prevent additional exposure risk to themselves. A boundary-isolation method was selected as the most effective technique for excluding Herbicide Orange from those areas where personnel were concentrated. This concept appeared to have the greatest possibility of success with the least interference with working personnel. The objective was to isolate Herbicide Orange within set boundaries, control access to those areas, and to eliminate carrying of the waste across the boundaries by ship or test personnel. The ship was, therefore, divided into clean and contaminated areas with boundaries separating them.

- Three areas of the ship were considered to be probable sources of contamination:
    1) The main deck (forward) which covered the waste storage tanks. Filling ports and access hatches (Butterworths) protrude through this deck from the tanks.
    2) The pump room, located below decks, aft of the waste storage area and below the living quarters.
    3) The combustion room, which houses the lower portions of the two furnaces, the burners, and the combustion control area.
- One area was designated as free of contamination. This area contained:
    1) The bridge, with ship control and radio communication.
    2) Living quarters for officers, crew, and test team.
    3) The galley and combined mess hall/recreation room.

In addition to defining the boundary-isolation method for controlling personnel movement, the personnel protection plan also defined criteria for interrupting the incineration to prevent exposure to Herbicide Orange. These criteria are discussed in Appendix A. In brief, the personnel protection plan provided for interruption of incinerator operations if:

- Conditions prevented keeping the plume off the ship
- Major spills occurred which could not readily be contained or cleaned
- Combustion efficiency fell below 99.9%
- Concentrations of 2,4-D + 2,4,5-T in the combustion effluent exceeded 130 ppm (130 $\mu g/m^3$) as determined by onboard analysis
- Workspace air concentrations of 2,4-D + 2,4,5-T exceeded the TLV of 10 ppm over 8 hours or 2 ppm over 16 hours as determined by onboard analysis

5.2 IMPLEMENTATION OF THE PERSONNEL PROTECTION PLAN

The following goals were set for personnel protection onboard the M/T Vulcanus:

- Isolating Herbicide Orange in working areas and excluding it from living areas by defining boundaries between dirty and clean areas
- Eliminating potential contamination carriers by providing for decontamination at these boundaries
- Locating and controlling contamination in a timely manner
- Controlling and monitoring incinerator operations to prevent workspace air concentrations of 2,4-D and 2,4,5-T in excess of TLVs.

Concepts developed in the Safety Plan were implemented by the test team and the ship's officers and crew. Implementation of the personnel protection procedures was effected by:

- A detailed briefing of ship and test personnel explaining the need for following the procedures by all personnel and the boundary-isolation concept
- Providing adequate and comfortable disposable protective clothing and a shower at the port exit from the combustion room
- Providing for an onboard analytical chemistry capability for detecting the spread of contamination past set boundaries and workspace air concentrations in excess of TLVs.

Briefing of the crew of the M/T Vulcanus was carried out at Gulfport, MI, just prior to loading the ship with Herbicide Orange. The briefing covered the toxic properties of Herbicide Orange, the need for personal hygiene, and the effectiveness of safety procedures in preventing exposure. Test personnel were similarly briefed. All personnel who might have come into contact with Herbicide Orange were given pre- and post-program physical examinations.

Protective clothing consisted of cellulose fiber coveralls and plastic shoe covers. The coveralls were light, porous, comfortable and inexpensive. They were discarded after each shift. Fresh coveralls were issued at the beginning of each shift. Shoe covers were available at the exits from the living quarters and at the port entrance to the combustion room. Disposal cans for used coveralls and shoe covers were provided in the shower area just inside the boundary. These cans were emptied daily and their contents burned.

A shower was installed in the combustion room at the port entrance just off the main deck (Figure 17). Soap, cotton-tipped swabs, powder, and fungicide were available. The water from the shower drained off the ship and into the ocean. The shower was for use by personnel going off duty from the combustion room or from other contamination sources, such as the pump room or storage area.

An onboard analytical chemistry capability was discussed in Section 4.2.9. An extensive sampling and monitoring program was followed. To detect the spread of contamination or excessive workspace air levels of herbicide, onboard gas chromatographic analyses of the following types of samples were performed:

- Areas critical with respect to the spread of contamination or likely to be sources of contamination were wiped with filter paper discs and then analyzed.
- Workspace air samples were taken by gas sampling syringes and analyzed.
- Portions of USAF-OEHL benzene impinger train samples were analyzed after each stack sampling test.

In addition, combustion efficiency was measured daily in order to determine that the permit requirement of at least 99.9% efficiency was met.

Monitoring activities included continuous workspace air samples (Section 3.4.1) and ship's drinking water. These samples were analyzed after each burn on Johnston Island.

5.3 RESULTS

Descriptions of the sampling techniques and equipment, analytical methodology, and results of the analyses used to implement the personnel protection plan are given in Sections 3 and 4. Analytical results and their implications with respect to the personnel protection plan are discussed in following sections.

5.3.1 Wipe Samples

Examination of suspected areas of contamination was carried out by wiping sections of the deck, walkways, and walls with filter paper. The wipes were placed in individual screw cap bottles and subjected to gas chromotographic analysis for 2,4-D and 2,4,5-T. Figure 17 shows the location of the wipe samples on a plan view of the M/T Vulcanus. Results of these analyses, given in detail in Table 44 (first burn), Table 45 (second burn), and Table 46 (third burn) show that good segregation of the herbicide was achieved during the first burn and that the galley and living quarters were free of herbicide.

However, because of minor spills (Section 5.5.2) during tank sampling before the second burn, the main deck around tank access hatches became contaminated. The presence of waste in living quarters and entry passageways was immediately detected by wipe sampling (Table 45). Scrubbing the interior floors and hosing the passageways reduced herbicide in these areas to below detection limits.

The presence of TCDD-free herbicide was detected in living quarters and entry passageways during the third burn (Table 46). This contamination was caused by minor spills of TCDD-free herbicide (Section 5.5.2). The amounts of TCDD-free herbicide found were very low, estimated to be <10 $\mu g/m^2$.

5.3.2 Workspace Air Monitors

Workspace air was monitored in the dining room, combustion room, pump room, and portable laboratory. These samples were analyzed, and the results are given in Tables 39 and 40.

Results of the analyses show that concentrations of herbicide in the four areas monitored were low, from 0.06 to 174 $\mu g/m^3$, during all three burns. Highest concentrations were found in the pump room, a not unexpected situation. In chemical tankers, this room is the chief source of fumes from the cargo being handled. The permitted concentrations of Herbicide Orange of 2.0 mg/m^3/16 hours and 10.0 mg/m^3/8 hours are greater than 1 order of magnitude above the concentrations found in the pump room, where personnel exposure was infrequent and of short duration.

In the combustion room, where the ambient temperatures were 200^{0}F in some areas, the permitted concentrations of herbicide were greater than 1 order of magnitude above the measured values. In the living area and portable laboratory, the permitted concentrations of herbicide were 3 to 4 orders of magnitude above the measured values. In all areas tested, it is evident that personnel were adequately protected with a large safety factor from toxic levels of Herbicide Orange in workspace air.

5.3.3 Potable Water Samples

Table 42 presents results of analyses of three samples of the drinking water used during the three burns. No herbicide could be detected at a detection limit of less than 0.1 ppb.

5.4 PLUME CHARACTERISTICS AND CONTROL

The Safety Plan (Appendix A) defined a responsibility for maintaining a speed and heading of the M/T Vulcanus so as to prevent contact of the plume with the ship.

Experience during the burning of organochlorine wastes by the M/T Vulcanus in the Gulf of Mexico and during the Herbicide Orange burns off Johnston Island showed that certain relative wind conditions and ship headings affected the direction and behavior of the plume and were effective in keeping it off the ship.

Visual location of the plume during the herbicide incineration was difficult because it was generally transparent and could only be seen close to the furnaces as a convection disturbance in the atmosphere. However, the plume was made visible as desired by the addition of NH_3 gas at the stack level. HCl measurements were also used to detect the plume, even though it could not be seen. A Drager apparatus consisting of an aspirating bellows and a standard color developing tube was used to identify and locate the plume by its HCl content.

A series of experiments was performed in order to study and measure the effect of wind speed, wind direction, ship heading, and propeller rpm on the plume. The results are summarized in Table 48. They appear to be a useful basis for plume control during at-sea incinerations.

In these experiments the ship was positioned in a particular attitude (heading) to the wind, the wind speed measured with an anemometer, and tests made for HCl on the downwind part of the ship. HCl was used as a convenient tracer for the plume.

When HCl was noted on the ship, even at the detection limit of 0.1 ppm, the contemporary conditions of ship heading, wind speed, and propeller rpm were considered unacceptable. The following observations were made:

- Drifting with the wind at 90 degrees directly abeam showed no HCl and thus no plume impingement onboard at wind speeds up to and including 10 m/s (20 knots). Incineration under these conditions may, therefore, be permitted.

TABLE 48. HYDROGEN CHLORIDE (HCl) IN AIR ONBOARD M/T VULCANUS

Date	Time	Location	Relative Humidity %	Ship Heading	Wind Dir. and Speed	Temp °C/°F	Barometer (mb)	Conc. HCl (ppm)	Notes
7/14/77	1600	Port, Comb Deck	84	340°	080°-8 m/s	27.2/81	1012.2	0	Drifting
	2000	Port, Main Deck	80	340°	060°-10 m/s	26.7/80	1012.2	0	Drifting
7/15/77	0800	Port, Comb. Deck	88	360°	100°-12 m/s	26.7/80	1012.5	2.0	Drifting
	1000	Port, Comb. Deck	84	005°	100°-10 m/s	26.7/80	1012.5	0	Drifting
7/16/77	0800	Port, Comb. Deck	88	348°	075°-8 m/s	26.1/79	1014.5	0	Drifting
	1600	Comb. Rm Fwd	84	350°	060°-8 m/s	26.7/80	1013.8	0	Drifting
		Comb. Rm Rear	84	350°	060°-8 m/s	26.7/80	1013.8	0	Drifting
7/17/77	0940	Port, Main Deck	88	360°	065°-10 m/s	26.7/80	1014.8	0	Drifting
	1600	Port, Comb. Deck	80	360°	070°-9 m/s	27.2/81	1013.0	0	Drifting
7/18/77	1020	Port, Main Deck	82	360°	090°-11 to 20 m/s	28.3/83	1014.0	0.5	Drifting
	1020	Comb. Room	82	360°	090°-11 to 20 m/s	28.3/83	1014.0	0.5-1.0	Drifting
	2030	Fantail	84	150°	105°-12 m/s	26.7/80	1014.5	2.0	40 RPM*
	2040	Fantail	84	160°	105°-12 m/s	26.7/80	1014.5	0	40 RPM
	2400	Fantail	84	160°	100°-12 m/s	26.1/79	1014.5	0	40 RPM
7/19/77	1000	Fantail	82	045°	090°-16 m/s	27.2/81	1014.0	3.0	40 RPM
	1010	Fantail	82	035°	090°-16 m/s	27.2/81	1014.0	0	40 RPM
	1400	Fantail	78	040°	080°-12 m/s	27.5/81.5	1014.0	2.0	40 RPM
	1410	Fantail	78	030°	080°-12 m/s	27.5/81.5	1014.0	0	40 RPM
7/20/77	0800	Port, Main Deck	86	350°	080°-9 m/s	26.7/80	1015.3	0	Drifting
	2200	Port, Main Deck	88	360°	085°-9 m/s	26.7/80	1014.9	0	Drifting
7/21/77	0800	Port, Comb. Deck	86	350°	075°-8 m/s	26.7/80	1015.0	0	Drifting
	2000	Port, Comb. Deck	82	345°	055°-9 m/s	26.9/80.5	1013.9	0	Drifting
7/22/77	0800	Port, Boat Deck	84	330°	050°-7 m/s	26.7/80	1014.5	0	Drifting
	1800	Port, Boat Deck	84	350°	060°-8 m/s	26.7/80	1013.0	0	Drifting
7/23/77	0800	Port, Comb. Deck	84	005°	095°-8 m/s	26.7/80	1014.3	0	Drifting
	1800	Starboard, Comb. Deck	84	140°	080°-6 m/s	26.7/80	1012.4	10.0	103 RPM
	1810	Starboard, Comb. Deck	84	150°	080°-6 m/s	26.7/80	1012.4	2.0	103 RPM
	1820	Fantail	84	150°	080°-6 m/s	26.7/80	1012.4	0	103 RPM
	1830	Starboard, Comb. Deck	84	155°	080°-6 m/s	26.7/80	1012.4	4.0	103 RPM
	1840	Starboard, Comb. Deck	84	150°	080°-6 m/s	26.7/80	1012.4	0	75 RPM
	1850	Starboard, Comb. Deck	84	150°	080°-6 m/s	26.7/80	1012.4	0	75 RPM
	1900	Starboard, Comb. Deck	84	150°	080°-6 m/s	26.7/80	1012.4	0	75 RPM

*Ship propeller rotational velocity

- Differences of from 50 to 90 degrees between the wind direction and the ship's heading apparently avoided plume contact with the ship when the propeller speed was held to 40 rpm and when the wind speed was greater than 20 knots. This condition held true for either side of the ship. Some degree of maneuverability of the ship was thus possible while avoiding plume impingement.

- In one limited set of experiments (Table 48), the plume was successfully kept off the fantail by a 70-degree wind-heading difference, at a propeller speed of 103 rpm. However, based on HCl measurements, the plume appeared to impinge on the usually unoccupied combustion deck. This situation was not acceptable. When the propeller speed was reduced to 75 rpm, the plume left the ship entirely at a heading difference of 70 degrees.

Results of these experiments are summarized schematically in Figure 18 which shows ship headings relative to wind direction which avoided plume impact. For example, with the wind direction off the port side of the ship, relative headings from 50 to 90 degrees (wind directly abeam) avoided plume impact. This figure was developed during the first burn and was used for proper ship orientation during the second and third burns.

5.5 INCIDENTS

5.5.1 Plume Impingements

There were several occasions of plume impingement or eddying of the plume on the ship. During the first burn, plume impingements resulted from flame extinguishment by layers of water floating on top of the waste in certain tanks. During the third burn, there were several occasions when the plume partially eddied onto the ship because of high wind velocity and somewhat erratic wind direction.

The first incident occurred at 9:50 a.m. on July 20 during the first burn. It was caused by a flameout in both incinerators which resulted in the expulsion of dense white fumes from the incinerator stacks. The resultant vapors

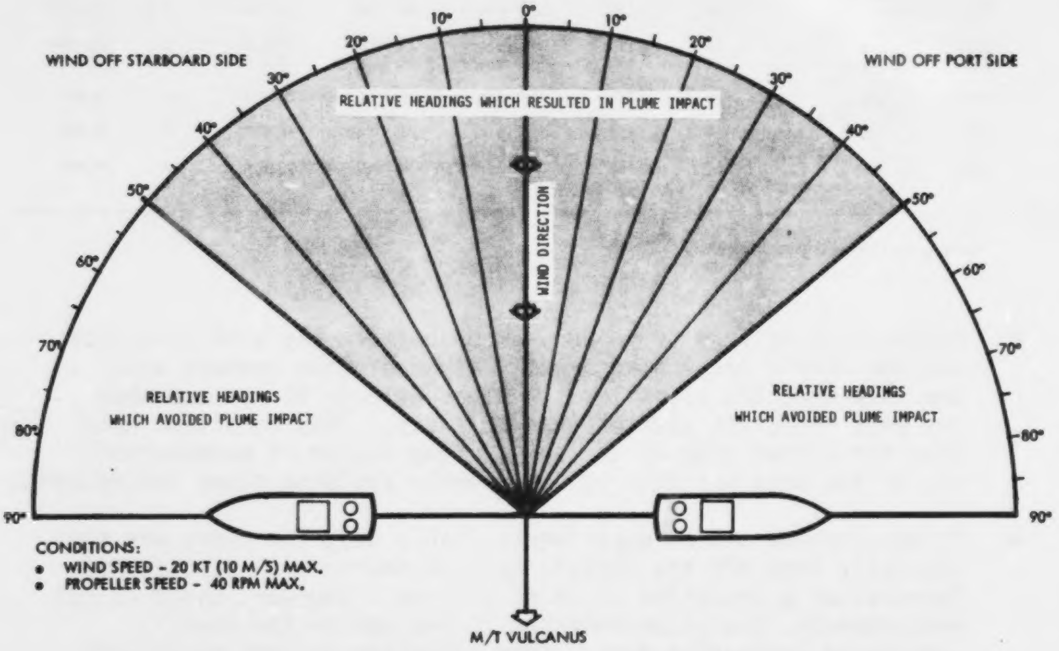
WIND OFF STARBOARD SIDE
WIND OFF PORT SIDE
0°
10°
20°
30°
40°
50°
60°
70°
80°
90°
RELATIVE HEADINGS WHICH RESULTED IN PLUME IMPACT
WIND DIRECTION
RELATIVE HEADINGS WHICH AVOIDED PLUME IMPACT
RELATIVE HEADINGS WHICH AVOIDED PLUME IMPACT
CONDITIONS:
• WIND SPEED - 20 KT (10 M/S) MAX.
• PROPELLER SPEED - 40 RPM MAX.
M/T VULCANUS

Figure 18. Ship headings relative to wind direction which avoided plume impact on ship.

impacted the port side of the ship for approximately 30 to 60 seconds. Because a porthole was open to the TRW quarters on the port side, the plume could have entered this living area. Wipe and syringe samples were taken from the TRW quarters and on the port side of the ship to determine the extent of contamination from the white plume. The syringe sample taken from the TRW quarters was negative for Herbicide Orange. Wipe samples were taken from the porthole sill and on areas just below and to either side of the porthole (the face of the refrigerator and the headboard of a bunk). The wipe taken from the porthole sill showed the presence of herbicide, all other areas tested negative. Decontamination was initiated by using high pressure saltwater to hose down the port companionway. The porthole sill in the TRW quarters was wiped with acetone and water. After decontamination, a wipe sample taken from the porthole sill showed no evidence of herbicide.

The second incident occurred at 4:20 a.m. on 21 July. A TRW team member was awakened by the odor of Herbicide Orange in the TRW quarters on the port side. The odor was immediately eliminated by opening the door to the galley which resulted in cross ventilation starboard to port. This incident was very brief and it is not clear whether it was caused by a momentary flameout or from the pump room vent.

A third incident occurred at 7:22 a.m. on 21 July as the result of a flameout. An oil-like fog was ejected from both stacks. The plume impinged on the port side of the ship and lasted about 15 to 20 seconds before a tank switchover was made by the ship's crew. The cause was traced to an aqueous layer floating on the top of the Herbicide Orange. Because of this incident, it was requested that the ship's officer put the ship underway just prior to emptying a tank. Wipe samples were taken, and the ship's crew repeated the hose-down of all affected areas on the port side. Samples that were taken proved to be negative, and a complete decontamination of the living area was not initiated.

The final flameout occurred at 2:55 a.m. on 23 July. This flameout was of very short duration (perhaps 5 seconds) and did not leave any measurable contamination on the ship.

All personnel onboard the Vulcanus were referred to the dispensary on Johnston Island at the end of the first burn. No effects were found.

During the debriefing on Johnston Island after the first burn, the problem of flameouts was discussed. Water layers that had caused the problem were analyzed and found to be 99% water, about 1% sodium salts of 2,4-D and 2,4,5-T, and about 80 ppm arsenic. All of this material remaining in the ship's tanks was consolidated into Tank 6P. A procedure for flashing (evaporating) this material during the second burn was developed and a stack gas sampling test was planned. The procedure was:

- The test was to be performed on the starboard incinerator. The burner nearest the wall thermocouples was to be shut off.
- Herbicide would be fed through the remaining two burners at a rate consistent with optimum incinerator performance. The flame temperature had to exceed the permit minimum of 1250°C.
- The water was to be fed into the third (off) burner, starting with a minimum feed rate.
- The following parameters were to be checked before increasing the water feed rate: flame temperature, wall thermocouple temperature, on-line instrumentation data, and appearance of the stack effluent.

In addition to the flashing procedure, a procedure to reduce the impact of flameouts was developed during the debriefing. This procedure was in effect during the second and third burns and called for:

- When nearing depletion of a tank, switch two of the three burners in each incinerator to a full tank, leaving one burner in each incinerator to complete emptying the first tank.
- Put the ship under power at a proper orientation to the wind direction (Figure 18).

There were no plume impingements during the second burn. During the third burn, there were several partial plume impingements when the plume eddied back onto the ship. These impingements were of short duration (10 to 30 seconds) and were caused by stormy weather during most of the burn. There was minimal personnel exposure, and post-program physical exams showed no effects.

5.5.2 Spills

There were several minor spills of herbicide during onboard operations. They were documented as they occurred. Figure 19 is a schematic of the Vulcanus' main deck showing cargo tank layout, tank hatches, and spill locations.

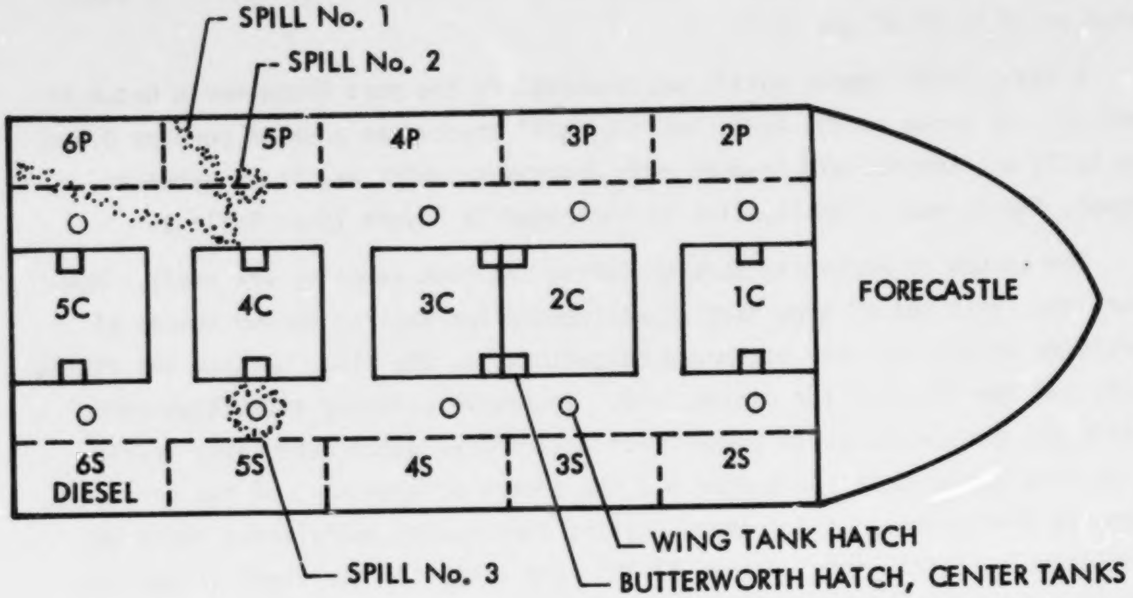
SPILL No. 1
SPILL No. 2
6P
5P
4P
3P
2P
5C
4C
3C
2C
1C
FORECASTLE
6S
DIESEL
5S
4S
3S
2S
WING TANK HATCH
SPILL No. 3
BUTTERWORTH HATCH, CENTER TANKS

Figure 19. Schematic of Vulcanus' main deck showing spill locations.

Solid lines in Figure 19 indicate above-deck-level platforms over the center tanks. The dashed lines indicate that the port and starboard wing tanks do not have these platforms.

No spills were observed during the first burn. At the time of sailing (13 July) what appeared to be a spill was noted on the main deck by the hatch cover of either Tank 4P or 5P. The area was sampled, cleaned, and resampled. Neither wipe sample showed the presence of herbicide.

After loading and before sailing for the second burn, samples of waste from the top, middle, and bottom of each tank were taken. A liter bottle was placed in a wire cage from which lead fishing weights were hung. A cord was attached to the neck of the bottle so it could be lowered into and raised from the tanks. A plug was inserted into the neck of the bottle. A cord was attached to the plug so the plug could be pulled when the bottle was in the correct position. After a sample was taken, the bottle and plug were removed from the tank. The cords were coiled on the deck around each hatch cover. The cords were saturated with Herbicide Orange. Therefore, the area around each hatch was subjected to a spill. The amount involved in these spills is estimated at 10 to 20 ml per spill.

A full, liter sample bottle was knocked off the port Butterworth hatch of Tank 4C. It broke on the deck, and the spill covered an area of perhaps 0.5 m^2. The spill was immediately covered with absorbant, which was later gathered, bagged, and burned. The location is indicated in Figure 19 as Spill 1.

The amount of herbicide spilled during the tank sampling was small. However, the first set of wipe samples analyzed after sailing showed traces of herbicide in the port and starboard companionways, the floor outside the dining room, and the floor of the dining room. Intensive cleaning activities were initiated, and herbicide in these areas was reduced below detectable levels. It is possible that the pump room was the source of some part of the herbicide found in living areas of the ship. During the loading operations, there was considerable traffic into and out of the pump room. If the usual at-sea precautions (coveralls and boot covers or separate pairs of shoes) were not observed during loading, then herbicide could have been carried out of the pump room and into other areas of the ship.

The same tank sampling activity was required prior to sailing for the third burn. Precautions to eliminate or reduce spills caused by tank sampling were taken. The U.S. EPA observer indicated there were no spills from this tank sampling.

TCDD-free herbicide (herbicide with a TCDD content below detection limits, 0.02 ppm) was stored in Tank 2C, the largest tank. During the third burn, each tank, after having been drained of waste herbicide, was rinsed by filling with TCDD-free herbicide. The waste tanks were rinsed serially. This procedure was intended to reduce residual waste herbicide by dilution with TCDD-free herbicide. The waste containing tanks were drained to dryness (observed by TRW and/or U.S. Air Force personnel) before rinsing.

During loading the ship with waste, the venting system was capable of equalizing pressure sufficiently rapidly so that hatch covers were dogged down tightly. During incineration, however, hatch covers had to be partially open, as the tank venting system apparently could not equalize pressure rapidly enough. Similarly, tank access hatches had to be open during tank rinsing operations.

During the third burn, there was another spill of herbicide, indicated as Spill 2 on Figure 19. At this time, the bow of the ship was riding high because several forward tanks were empty. The ship also had been given a steep list to port to help drain the tank which was then being emptied. The best recollection is that the spill came from Tank 4C which was filled with TCDD-free herbicide. The Butterworth hatch was open, and several sharp rolls spilled on the order of 10 to 20 liters of rinsate onto the deck. Because of the bow-high and port-list attitude of the ship, the spilled rinsate ran toward the rear of the ship, stopping at the entry to the port companionway. Shortly after the spill, the deck was washed with seawater. Wipe samples taken after the spill showed traces of herbicide (rinsate) in the designated clean areas of the ship. The living quarters and the port and starboard companionways were cleaned and resampled.

A much smaller spill of TCDD-free herbicide rinsate occurred from the hatch of Tank 5S. There was a slight list to starboard at the time. The tank was overfilled for the rolling conditions. Perhaps 0.5 to 1 liter of rinsate spilled onto the deck before filling could be stopped. The spill was flushed into the sea. This spill is indicated as Spill 3 in Figure 19.

Because every tank was filled with TCDD-free herbicide during the third burn, it is likely that the main deck around all hatch covers was contaminated. The rolling of the ship (the weather was bad and the seas were high) caused the tank contents to slosh vigorously. It is expected that small amounts of TCDD-free herbicide rinsate spray could have escaped from tanks as they became nearly full.

During all three burns, the waste tanks were gauged manually with a coiled steel tape. Drips of herbicide occurred despite the use of a rag to wipe the tape as it was removed from a tank.

The main deck thus appears to have been the source of contamination which was spread into other areas of the ship (see wipe sample results for 2 August and 29 August in Tables 46 and 47, respectively). The corrective action taken after herbicide appeared in the living quarters was effective.

5.6 SUMMARY OF SHIP CLEANLINESS MAINTENANCE

During the three burns of Herbicide Orange onboard the M/T Vulcanus, the following observations were made:

- Effective protection of operating and technical personnel from Herbicide Orange exposure was achieved by isolating the material from living areas and restricting it to operating areas. Minor amounts of herbicide were detected in the living area which was then readily decontaminated.
- There were no major exposures of personnel to Herbicide Orange during the three incinerations.
- There were no large spills nor leaks.
- The walkways along the port and starboard main deck passageways showed some contamination, which was easily hosed away.
- The principal source of contamination was the main deck about the waste tank access hatches. As discussed in Section 5.5.2, there were minor herbicide spills during tank sampling before the second and third burns. Herbicide from these spills apparently migrated into the living areas because of uncontrolled personnel movement.
- The disposable fiber coveralls and shoe covers appeared to be effective. Disposal of these by burning in the furnace was easily accomplished.
- The combustion room remained at a low level of contamination, indicating excellent housekeeping and high quality engineering practice.
- The pump room was a source of Herbicide Orange vapors.
- The flameouts were a source of contamination, since vaporized Herbicide Orange, left the stacks at a lower velocity and did not behave as a normal plume because of its density and lower temperature. Methods of controlling these flameouts were suggested (Section 5.5.1) and put into operation successfully.

6. WASTE DESTRUCTION EFFICIENCIES AND EMISSIONS ASSESSMENT

6.1 WASTE DESTRUCTION EFFICIENCIES

Results of analyses for 2,4-D and 2,4,5-T in the Lear-Siegler train samples are given in Table 30. Results of analyses by BCL for 2,4-D and 2,4,5-T in the benzene impinger train samples are given in Table 41. WSU analysis results for TCDD in the benzene impinger train samples are given in Table 38. These analytical results are expressed in terms of emission concentrations, e.g., $\mu g/m^3$.

The usual engineering method of calculating destruction efficiencies is in terms of rates,

$$DE = 100 \times \frac{\text{rate fed - rate emitted}}{\text{rate fed}}$$

Instead of recalculating analytically determined emission concentrations as emission rates, herbicide feed rates were converted to emission concentrations for destruction efficiency calculations. Converting herbicide (or TCDD) feed rates to emission concentrations was done by (1) calculating combustion effluent flow rates from combustion stoichiometry, on-line monitoring data, and herbicide (or TCDD) feed rates as illustrated in Appendix F.2 and (2) dividing herbicide (or TCDD) feed rates by combustion effluent flow rates as illustrated in Appendix F.8. These values for maximum herbicide (or TCDD) emission concentrations are termed emission concentrations at 0% destruction efficiency.

Table 49 gives maximum emission concentrations at 0% destruction efficiency for 2,4-D + 2,4,5-T and TCDD, waste feed rates, and combustion effluent flow rates. A sample calculation is given in Appendix F-10. Destruction efficiencies were calculated from:

$$DE = 100 \times \frac{C_o - C_F}{C_o}$$

TABLE 49. EMISSION CONCENTRATIONS OF 2,4-D + 2,4,5-T AND TCDD AT 0% DESTRUCTION EFFICIENCY*

				Emission Concentration at 0% DE	
Burn	Date	Waste Feed, Metric Tons/hr†	Combustion Effluent Flow Rate, m^3/hr	2,4-D + 2,4,5-T g/m^3	TCDD μg/m3
1	7/14/77	6.05	52,200	Fuel Oil Background Test	
1	7/15/77	6.05	50,970	119	±
1	7/16/77	7.03	60,900	115	2.47
1	7/18/77	7.46	62,000	120	‡
1	7/19/77	6.95	60,600	115	‡
1	7/23/77	7.28	61,400	119	‡
2	8/08/77	6.85	56,900	121	283
2	8/13/77	7.17	69,800	103	86.3
3	8/28/77	5.83*	51,900	112	284

*Sample calculation in Appendix F.8. See Appendix F.12 for conversion of μg/m^3 to ppb.

†Metric tons per hour per incinerator.

‡ These samples were not analyzed.

where

C_o = emission concentration of 0% destruction efficiency

C_F = emission concentration determined from analyses

Table 50 presents destruction efficiencies for TCDD calculated from the WSU analyses. Because TCDD was not detected in most of the samples, the destruction efficiencies in Table 50 are, in fact, greater than the table entries as indicated by the ">" character. It should be noted that the entries for the tests of 8 and 13 August indicate that TCDD destruction efficiencies were greater than 99.87% and 99.89%, respectively. Section 4.2.5 presented a discussion of the severe chemical interferences in the analyses of these samples. These interferences prevented attaining minimum detectable concentrations sufficiently low so that calculated destruction efficiencies would exceed 99.9%. For example, if the minimum detectable concentration of TCDD in the benzene impinger sample of 8 August had been <0.017 ng/ml rather than <0.034 ng/ml, then the calculated destruction efficiency would have been >99.9%.

Tables 51 and 52 present, respectively, destruction efficiencies for 2,4-D plus 2,4,5-T calculated from TRW and BCL analyses of combustion effluent samples. All calculated destruction efficiencies are greater than 99.999%, indicative of incineration well in excess of permit requirements. It is noteworthy that the TRW and BCL results for 2,4-D and 2,4,5-T were on samples from different sampling trains using different analytical procedures as discussed in Sections 4.2.2 and 4.2.6, respectively. These high destruction efficiencies for 2,4-D and 2,4,5-T give confidence that the destruction efficiency for TCDD was in excess of permit requirements.

Because of the possibility that chlorinated constituents of the waste could be degraded into and emitted as simpler organochlorine compounds, results of the GC/MS analyses (Table 30) of the Lear-Siegler train samples were examined for organochlorine compounds. Concentrations of these compounds were summed, and destruction efficiencies were calculated. Table 53 presents emission concentrations and destruction efficiencies of organochlorine compounds found in the Lear-Siegler train samples. It was assumed that the waste was totally composed of organochlorine compounds. It can be seen that the

TABLE 50. DESTRUCTION EFFICIENCIES FOR TCDD FROM WSU ANALYSES[*]

Sample	Sample Volume mℓ	Gas Volume m^3[†]	TCDD Concentration ng/mℓ[‡]	TCDD Emission Concentration ng/m^3	Destruction Efficiency %
HO-1-CF-714-F (feed)					
HO-1-BI-714-F	725	0.1129		Fuel Oil Background Test	
HO-1-LR-714-F	60.4				
HO-1-PR-717-F/H	2.2				
Total TCDD					
HO-1-CF-716-H (feed)			2.5×10^3		
HO-1-BI-716-H	725	0.1179	<0.00094	<5.8	
HO-1-LR-716-H	42.5		<0.045	<16	
HO-1-PR-717-F/H	2.3		<0.086	<1.7	
Total TCDD				<24	>99.99
HO-2-CF-808-H (feed)			$2.8 \times 10^{+3}$		
HO-2-BI-808-H	600	0.1962	<0.034	<102	
HO-2-LR-808-H	57.4		0.136	39.8	
HO-2-PR-808-H	10.7		3.34	182	
Total TCDD				<324	>99.89
HO-2-CF-813-H (feed)			$1.0 \times 10^{+3}$		
HO-2-BI-813-H	600	0.3249	<0.047	<86.1	
HO-2-LR-813-H	37.9		<0.11	<12.6	
HO-2-PR-813-H	14.6		<0.30	<13.5	
Total TCDD				<112	>99.87
HO-3-CF-828-H (feed)			$2.8 \times 10^{+3}$		
HO-3-BI-828-H	570	0.2266	<0.040	<101	
HO-3-LR-828-H	48.9		<0.012	< 2.7	
HO-3-PR-828-H	12.6		<0.048	< 2.7	
Total TCDD				<106	>99.96

[*] Sample calculation in Appendix F.9. See Appendix F.12 for conversion of ng/m^3 to ppt.

[†] Volume of stack gas sampled at 20°C and 1013.2 mbar.

[‡] Concentration of TCDD in sample. A less than ("<") indicates TCDD was not detected. The values are minimum detectable quantities.

destruction efficiency of the waste in terms of organochlorine compounds emitted was greater than 99.999%.

6.2 EMISSIONS ASSESSMENT

Emissions of volatile hydrocarbons were estimated from the C7-C16 GC analysis of the Lear-Siegler train samples, while the GC/MS analyses of these samples showed the presence of phthalate esters and/or silicones. These compounds were present in negligible amounts. Despite the uncertainties in the analytical data, the C7-C16 GC analytical results can be used with some degree of confidence to give estimates of the emissions of volatile hydrocarbons during the

TABLE 51. DESTRUCTION EFFICIENCIES FOR 2,4-D AND 2,4,5-T FROM LEAR-SIEGLER TRAIN ANALYSES*

			Concentration			
Sample	Sample Volume mℓ	Gas Volume m^{3†}	2,4-D µg/m^3	2,4,5-T µg/m^3	Total 2,4-D/2,4,5-T µg/m^3	Destruction Efficiency %
HO-1-ST-714-F		3.9262				
HO-1-LR-714-F	2098			Fuel Oil Background Test		
HO-1-PR-717-F/H	75					
Total						
HO-1-ST-716-H		6.0914	<0.3	<0.3	<0.6	
HO-1-LR-716-H	2191		<3	<3	<6	
HO-1-PR-717-F/H	116		<0.2	<0.2	<0.4	
Total					<7	>99.999
HO-2-ST-813-H		8.8333	<0.2	<0.2	<0.4	
HO-2-LR-813-H	1031		<0.9	<0.9	<1.8	
HO-2-PR-813-H	398		<0.4	<0.4	<0.8	
Total					<3	>99.999
HO-3-ST-828-H		6.8847	<0.3	<0.3	<0.6	
HO-3-LR-828-H	1485		<4	<4	<8	
HO-3-PR-828-H	383		<60	<60	<120	
Total					<130	>99.999

---

*Sample calculation given in Appendix F.10. See Appendix F.12 for conversion of µg/m^3 to ppb.

†Volume of combustion effluent sampled, dry gas at 20°C and 1013.2 mbar.

<Indicates not detected.

TABLE 52. DESTRUCTION EFFICIENCIES FOR 2,4-D AND 2,4,5-T FROM BCL ANALYSES*

Sample	Sample Volume mℓ	Gas Volume m³†	2,4-D μg/m³	2,4,5-T μg/m³	2,4-D + 2,4,5-T μg/m³	Destruction Efficiency %
HO-1-BI-714-F	600	0.1116			Fuel Oil Background Test	
HO-1-LR-714-F	59.74					
HO-1-PR-717-F	2.13					
Total						
HO-1-BI-715-H	600	0.1262	<380	<190	<570	
HO-1-LR-715-H	42.14		<6.8	<3.3	<10	
HO-1-PR-717-H	2.41		‡	‡	-	
Total					<580	>99.999
HO-1-BI-716-H	6[illegible]	0.1211	<400	<200	<600	
HO-1-LR-716-H	43.62		<7.2	<3.6	<11	
HO-1-PR-717-H	3.08		‡	‡	-	
Total					<610	>99.999
HO-1-BI-718-H	600	0.1235	<390	<190	<580	
HO-1-LR-718-H	43.28		<7.0	<3.5	<11	
HO-1-PR-722-H	3.08		<1.5	<0.8	<2.2	
Total					<590	>99.999
HO-1-BI-719-H	600	0.1059	<450	<230	<680	
HO-1-LR-719-H	40.78		<7.7	<3.9	<12	
HO-1-PR-722-H	2.66		<1.5	<0.8	<2.3	
Total					<690	>99.999
HO-1-BI-723-H	600	0.1058	<450	<230	<680	
HO-1-LR-723-H	29.74		<5.6	<2.8	<8.4	
HO-1-PR-725-H	6.46		<3.7	<1.8	<5.5	
Total					<690	>99.999
HO-2-BI-813-H	600	0.2788	<170	<86	<260	
HO-2-LR-813-H	32.5		<2.3	<1.2	<3.5	
HO-2-PR-813-H	12.5		<4.5	<1.3	≤5.8	
Total					<270	>99.999
HO-3-BI-828-H	610	0.2811	<170	<87	<260	
HO-3-LR-828-H	46		<3.3	<1.6	<4.9	
HO-3-PR-828-H	11		<1.6	<0.8	<2.3	
Total					<270	>99.999

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*Sample calculation in Appendix F.11. See Appendix F.12 for conversion of μg/m³ to ppb.

†Volume gas sampled at 20°C and 1013.2 mbar.

‡This sample was inadvertantly not given to BCL for analysis.

TABLE 53. DESTRUCTION EFFICIENCIES OF ORGANOCHLORINE COMPOUNDS

Sample	Emission Concentration $\mu g/m^3$	Destruction Efficiency %
HO-1-ST-714-F	<0.5	Fuel Oil
HO-1-LR-714-F	<4	Background Test
TOTAL	<4	
HO-1-ST-716-H	6	
HO-1-LR-716-H	<18	
HO-1-PR-716-H	<0.2	
TOTAL	<24	>99.999
HO-2-ST-813-H	30	
HO-2-LR-813-H	<1	
HO-2-PR-813-H	<0.2	
TOTAL	<31	>99.999
HO-3-ST-828-H	66	
HO-3-LR-828-H	<2	
HO-3-PR-828-H	50	
TOTAL	<120	>99.999

"<" means not detected.

four tests from which samples were analyzed. These estimates are given in Table 54. They should be considered upper bounds, that is, overestimates of emissions of volatile hydrocarbons.

Analyses of the Lear-Siegler train samples (Table 30) showed that they were quite complex. Trichlorophenol, a minor herbicide constituent, was found in the sorbent trap of 13 August 1977 and was the only herbicide constituent found in any Lear-Siegler train sample.

Aromatic hydrocarbons were shown to be present in the combustion effluent samples [illegible] the GC/MS analyses. The only reasonable source of these compounds was synthesis in the flame because they were not constituents of the

TABLE 54. ESTIMATES OF VOLATILE HYDROCARBON EMISSIONS*

Sample	Emissions mg/m^3	Total for Test, mg/m^3	Destruction Efficiency, %
HO-1-ST-716-H	0.35		
HO-1-LR-716-H	12.1		
HO-1-PR-716-H	7.8		
		14	99.98
HO-2-ST-813-H	0.85		
HO-2-LR-813-H	3		
HO-2-PR-813-H	26		
		30	99.97
HO-3-ST-828-H	<0.2		
HO-3-LR-828-H	11		
HO-3-PR-828-H	3.4		
		14	99.99

*See Appendix F.12 for conversion of mg/m^3 to ppm.

waste nor are they common contaminants. Quantitation of the GC/MS data was accurate to ± factor of 10. Greater quantitative accuracy was not planned. Estimates of emissions of aromatic hydrocarbons can be obtained from the GC/MS analyses. Table 55 presents these estimates.

Destruction efficiencies for 2,4-D plus 2,4,5-T were all in excess of 99.999%, indicative of highly efficient incineration. Destruction efficiencies for TCDD were greater than 99.9% for two of the tests and greater than 99.87% and 99.89% for two other tests. Because of the very high destruction efficiencies for 2,4-D and 2,4,5-T and the chemical interferences in the TCDD analyses, it is probable that the destruction efficiencies for TCDD were similarly very high and certainly in excess of 99.9%.

TABLE 55. ESTIMATES OF EMISSIONS OF AROMATIC HYDROCARBONS*

Sample	Emissions $\mu g/m^3$	Total for Test $\mu g/m^3$	Destruction Efficiency, %
HO-1-ST-716-H	<0.3		
HO-1-LR-716-H	130		
HO-1-PR-716-H	<0.1		
		130	>99.999
HO-2-ST-813-H	27		
HO-2-LR-813-H	0.9		
HO-2-PR-813-H	<0.4		
		30	>99.999
HO-3-ST-828-H	29		
HO-3-LR-828-H	240		
HO-3-PR-828-H	190		
		460	>99.999

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*See Appendix F.12 for conversion of $\mu g/m^3$ to ppb.

7. ERROR PROPAGATION ANALYSIS OF DESTRUCTION EFFICIENCY CALCULATIONS

This section briefly summarizes a detailed error propagation analysis, presented in Appendix G, of destruction efficiency calculations used in this report. The error analysis shows that destruction efficiencies are determined by the following variables: oxygen, carbon dioxide, and carbon monoxide in the combustion effluent; composition of the waste feed; and emission concentrations of waste constituents determined by laboratory analyses of combustion effluent samples. Appendix G also shows that as long as there is excess air, minor variations in combustion air and waste feed rates do not affect destruction efficiency because it is a dimensionless ratio. Variances in destruction efficiencies for 2,4-D + 2,4,5-T and TCDD were calculated from the variances in the factors listed above. Average values and standard deviations of the variables are presented in Table 56.

Results of the error propagation analysis in Appendix G are summarized as follows:

- For 2,4-D + 2,4,5-T
    1) The mean, $\overline{DE}$, and standard deviation, s(DE), in destruction efficiency for 2,4-D + 2,4,5-T are:

       $\overline{DE} = 99.999971\%$

       $s(DE) = 4.5 \times 10^{-5}\%$

    2) A conservative statistical analysis shows that there is 95% confidence that not more than 1 measured destruction efficiency in 1000 would be less than 99.99935%.

TABLE 56. SUMMARY OF VARIABLES FOR ERROR ANALYSIS*

Variable		Units	Mean	Standard Deviation
a	Weight fraction 2,4-D+2,4,5-T in herbicide	dimensionless	0.8599	0.0547
b	Emission concentration of 2,4-D+2,4,5-T	metric ton/m^3	46.7×10^{-12}	72.2×10^{-12}
d	Weight fraction TCDD in herbicide	dimensionless	1.916×10^{-6}	7.23×10^{-7}
e	Emission concentration of TCDD	metric ton/m^3	1.859×10^{-13}	1.42×10^{-13}
$C\ell/C$	Chlorine/carbon ratio in waste	dimensionless	0.5834	0.0018
$\%O_2$	Oxygen content of combustion effluent	%	8.9	1.4
$\%CO_2$	Carbon dioxide content of combustion effluent	%	10.3	1.7
K	Second order variable	moles	0.4144	-
K'	Second order variable	moles	21.57	-

- For TCDD

  1) The mean, $\overline{DE}$, and standard deviation, s(DE) in destruction efficiency for TCDD are:

     $\overline{DE}$ = 99.948%

     s(DE) = 0.044%

  2) A conservative statistical analysis shows that there is 95% confidence that not more than 1 measured destruction efficiency in 1000 would be less than 99.54%.

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APPENDIX A

SAFETY PLAN
FOR
INCINERATION OF HERBICIDE ORANGE
ON BOARD THE M/T VULCANUS

SAFETY PLAN
FOR
INCINERATION OF HERBICIDE ORANGE
ON BOARD THE M/T VULCANUS

Prepared by:
TRW Inc.
Contract No. 68-10-2966
EPA Project Officer: Dr. Ronald Venezia

Revision No. 2: 5 May 1977

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SAFETY PLAN
FOR
INCINERATION OF HERBICIDE ORANGE
ON BOARD THE M/T VULCANUS

EPA Permit No. 770DH001R

Dated 25 April 1977

REVISED: 5 May 1977

U.S. Environmental Protection Agency

Washington, D.C.

PREFACE

The draft Comprehensive Safety Plan, set forth in Appendix 14 of the Herbicide Orange hearing record of April 7, 1977, was reviewed and revised at a joint EPA, U.S.A.F., TRW and OCS meeting which was held at Gulfport, Mississippi, on May 5, 1977. This document which includes the modifications agreed to at the Gulfport meeting is the final plan and has been entered into the record as Appendix 14. Verbal approval of the final Safety Plan was given by Lt. Col. John Gokelman, U.S.A.F., on May 17 and by Dr. Ronald A. Venezia, EPA on May 16, 1977.

If newly acquired scientific data indicate that additional safety provisions or criteria should be included in the plan, EPA, after consultation with the U.S.A.F. and TRW, will establish such additional provisions or criteria.

Russel H. Wyer, P.E.
Deputy Director
Oil & Special Materials Control
Division

May 19, 1977

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SAFETY PLAN
FOR
INCINERATION OF HERBICIDE ORANGE
ON BOARD THE M/T VULCANUS

1. PURPOSE AND SCOPE

The purpose of this document is to define a plan to ensure the safety of personnel participating in the incineration of Herbicide Orange on board the M/T Vulcanus. All personnel on board ship will adhere to the provisions of this plan during all phases of the anticipated three incineration burns. TRW will brief officers and crew members of the M/T Vulcanus with this safety plan data and procedures. This is particularly important with regard to personal hygiene, equipment malfunctions, spills and criteria for terminating a given burn. Due to the inherent confinement while at sea, and required interaction of TRW and Vulcanus personnel, a thorough understanding of the contents of this document is mandatory on the part of all concerned.

The scope of the safety plan is limited to shipboard operations. Specifically excluded are the safety requirements for Herbicide Orange de-drumming, drum cleaning and ship loading operations, which are covered by U.S. Air Force, U.S. Coast Guard and M/T Vulcanus standard procedures.

To assist in establishing and maintaining safety procedures and routines, TRW will designate a Safety Director for ocean incineration operations. This individual will be a member of the TRW sampling and monitoring team. His duties will include: safety procedure briefing of all ship's personnel; monitoring the implementation of this safety plan; and advising the TRW crew leader, ship's master and Air Force representative regarding corrective action for unsafe conditions or incidents.

2. POTENTIAL HAZARDS

The Herbicide Orange requiring disposal is a viscous, clear amber orange liquid containing 50 percent (±1.5%) by volume of the normal butyl ester of 2,4-dichlorophenoxyacetic acid (2,4-D) and 50 percent (±1.5%) by volume of the normal butyl ester of 2,4,5-trichlorophenoxyacetic acid (2,4,5-T). The highly toxic contaminant present in Herbicide Orange is 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD). The U.S. Air Force has analyzed the Herbicide Orange stocks and found TCDD concentrations ranging from 0.05 to 47.0 ppmw. Statistical evaluation of these data indicated that pooled stocks would have an estimated average TCDD concentration of 1.9 ppmw (±0.7 ppmw) at 95 percent confidence level.

The principal Herbicide Orange constituent of concern, TCDD, has been found to be highly embryotoxic, teratogenic* and acnegenic and is lethal in the microgram-per-kilogram of body weight range. The detailed toxicological properties of TCDD, as compiled by the U.S. Air Force, are described in Reference 1. The no-effect TCDD dose levels for embryotoxicity and chick endema are 0.03 to 0.1 μg/kg/day respectively. Assuming that a person inhales 30 m^3 of air in a 24-hr day and a body weight of 60 kg for an average person, the amount of TCDD absorbed into the blood stream of a person will be less than 0.03 μg/kg X 60 kg = 1.8 μg if the ambient concentration of TCDD is less than 1.8/30 = 0.06 $\mu g/m^3$, even if the efficiency of pulmonary absorption is 100 percent. Thus an ambient TCDD concentration of 0.06 $\mu g/m^3$ may be considered as the no effect level for humans. With the application of an additional safety factor of 10, it is proposed that 6 ng/m^3 be considered as the safe ambient concentration for TCDD for all personnel on board the M/T Vulcanus.

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*Teratogenic - tending to cause developmental malfunctions and monstrosities.

1. U.S. Air Force Report, "Amendment to Final Environmental Statement on the Disposition of Herbicide Orange by Incineration," October 1976.

The two major constituents of Herbicide Orange, the butyl esters of 2,4,-D and 2,4,5-T, are of moderate toxicity to mammals. The acute oral and dermal LD_{50}* values of the 2,4-D acid to the rat have been reported to be 375 and 1500 mg/kg body weight respectively. The acute oral LD_{50} of mixed butyl esters of 2,4-D to rats is 620 mg/kg. The acute oral LD_{50} of the 2,4,5-T acid to rats is 500 mg/kg. Chronically, both 2,4-D and 2,4,5-T are of low toxicity, because of the highly developed kidney function possessed by mammals that will rapidly eliminate 2,4-D and 2,4,5-T by active tubular secretion. Thus, the cumulative effects of 2,4-D and 2,4,5-T are minimal. The American Conference of Governmental Industrial Hygienists (ACGIH) recommended Threshold Limit Values (TLV) for either 2,4-D or 2,4,5-T is 10 mg/m^3. The TLV is a time-weighted safe air concentration for an 8-hour work day or 40-hour work week. Based upon the TLV, a range of time limited ambient (personnel breathing zone) concentrations considered safe exposure levels for personnel on board the M/T Vulcanus is as follows:

Combined Concentrations of Butyl Esters of 2,4-D, 2,4,5-T

2.0 mg/m^3 for samples taken periodically over 16 hours, or
10.0 mg/m^3 for samples taken periodically over 8 hours.

The detailed toxicological properties of 2,4-D and 2,4,5-T, as compiled by the U.S. Air Force, are described in Reference 1. In addition to the toxicological hazards, Herbicide Orange is also flammable.

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*LD_{50} - Lethal dose fifty. A calculated dose of a chemical substance which is expected to cause the death of 50% of an entire population of an experimental animal species, as determined from the exposure to the substance, by any route other than inhalation, of a significant number from that population.

3. CRITERIA FOR TERMINATION OF A BURN

Due to the highly toxic nature of the TCDD contaminant present in Herbicide Orange, the TRW team leader acting on behalf of the U.S. Environmental Protection Agency, shall, in consultation with the cognizant U.S. Air Force representative, retain the authority to terminate and/or initiate incineration. The criteria that will be used by the TRW team leader to measure safe shipboard operation are summarized in Table 3.1 and discussed in the following sections. These criteria will only be used as guidelines. It should be recognized that, in addition to the TRW team leader, authority to terminate any individual incineration test shall also rest with any one of the following personnel: U.S. Air Force designate, or the captain of the M/T Vulcanus.

3.1 PLUME IMPINGEMENT

The plume arising from the incinerator stacks will be injected with ammonia as required to make it visible as necessary. Incineration with Herbicide Orange will be terminated and shipboard personnel will be withdrawn to a safe area, if at any time during the test, the plume is observed to remain on the deck of the M/T Vulcanus even after corrective measures have been attempted.

3.2 HERBICIDE ORANGE SPILLS

Incineration will be terminated if a spill occurs on board the M/T Vulcanus and cannot be readily contained or cleaned.

3.3 COMBUSTION EFFICIENCY

The CO and CO_2 levels determined at or near the exit plane will be used as an indication of overall combustion efficiency using the following equation:

$$\%\ \text{Combustion Efficiency} = \frac{\text{CO}_2\ \text{concentration} - \text{CO concentration}}{\text{CO}_2\ \text{concentration}} \times 100$$

Combustion efficiencies in excess of 99.9 percent are deemed necessary as an indication that high destruction efficiencies for Herbicide Orange constituents

TABLE A-1. CRITERIA FOR TERMINATION OF A BURN*

Observation/ Measurement	Decision Criteria	Action to be Taken
Plume Impingement	Plume is observed to remain on the deck of the M/T Vulcanus even after evasive action	Termination of incineration and withdrawal of shipboard personnel to a safe area.
Herbicide Orange Spills	Large spills that cannot be readily contained.	Termination of incineration and withdrawal of shipboard personnel to a safe area.
Combustion Efficiency	Combustion efficiency less than 99.9%	Termination of incineration.
On Board Determination of 2,4-D/2,4,5-T in Stack Gas	Combined 2,4-D/2,4,5-T concentration in excess of 130 mg/m^3 in the stack gas.	Termination of incineration
On Board Determination of Ambient Level for 2,4-D/2,4,5-T	Combined ambient (personnel breathing zone) level of 2,4-D/2,4,5-T in excess of 2.0 mg/m^3 over 16 hr. or 10 mg/m^3 over 8 hr.	Termination of incineration and/or immediate withdrawal of shipboard personnel to a safe area.

*The TRW team leader will consult with the U.S. Air Force designate before taking any action to terminate incineration. If appropriate, fuel oil may be substituted as a fuel while corrective action is being taken.

may be anticipated. The 99.9 percent combustion efficiency corresponds to approximately 100 ppm CO in the combustion product gas. The detection of large amounts of CO in the stack gas (and hence lower combustion efficiency) is an indication that incomplete combustion is taking place in the incinerator. Incineration will be terminated if the combustion efficiency is less than 99.9 percent.

3.4 ON BOARD DETERMINATION OF STACK EMISSIONS OF HERBICIDE ORANGE CONSTITUENTS

In addition to monitoring the CO and CO_2 levels in the stack gas, grab samples collected from the benzene impinger will also be directly injected into a GC equipped with a FID for 2,4-D and 2,4,5-T analyses by TRW. The GC/FID combination provides a lower detection limit of approximately 1.0 mg/m^3 for 2,4-D or 2,4,5-T in the stack gas. For on-board safety requirements, the allowable limit for combined 2,4-D/2,4,5-T concentration in the stack gas will be 130 mg/m^3 based upon a 99.9 percent destruction efficiency. The TLV for either 2,4-D or 2,4,5-T is 10 mg/m^3.

Incineration will be terminated if the combined 2,4-D/2,4,5-T concentration in the stack gas is in excess of 130 mg/m^3.

3.5 ONBOARD DETERMINATION OF AMBIENT LEVEL OF HERBICIDE ORANGE CONSTITUENTS

Ambient 2,4-D/2,4,5-T concentrations result from atmospheric dispersion of stack emissions as well as any fugitive emissions onboard the M/T Vulcanus. The TRW team leader will alert shipboard personnel and direct the location and elimination of such emission sources. Incineration will be terminated and/or shipboard personnel withdrawn if the combined ambient (personnel breathing zone) level of 2,4-D/2,4,5-T is in excess of 2.0 mg/m^3 over a 16-hour period, or in excess of 10 mg/m^3 over an 8-hour period.

4. PERSONNEL PROTECTIVE EQUIPMENT

Due to the potential health hazard relating to the sampling and monitoring of the incineration of Herbicide Orange aboard the M/T Vulcanus, special safety requirements have been established for all personnel to ensure that no hazards exist. To assure adequate protection, issued coveralls will be worn as appropriate during set-up, operation, and clean up of all sampling and/or monitoring equipment.

In addition to the normal equipment used in this type of activity, the following items will be provided.

1) NIOSH approved pesticide gas respirator.
2) Portable monitors, MSA Model 5 or S pumps fitted with sample tubes containing Chromosorb 102
3) Fire extinguishers

    Ansul - Model CD-5
    Sentry - Model SY-1012
4) Fire fighter entry suits
5) Scott air pak
6) Portable emergency eye baths

All personnel that will be onboard the M/T Vulcanus and may enter a potentially contaminated area will be duly trained on the proper use and operation of the above equipment.

Other general safety requirements that will be adhered to are the following:

1) All personnel within the incinerator area and/or sampling area during the incineration of Herbicide Orange will have an approved gas mask available for immediate use.
2) If an emergency condition is detected, all personnel will be notified to don masks and to evacuate a given area if necessary.

3) Personnel exposed to high temperatures and/or direct thermal radiation will wear entry suits.

4) Confirmed or suspected spills will be reported to the ship's master and the Safety Director for proper clean up.

5. PERSONAL HYGIENE

The observed effects on animals of tetrachlorodibenzo-p-dioxin (TCDD) or of 2,4,5-trichlorophenoxyacetic and n-butyl ester (2,4,5-T) containing TCDD are described in detail in Reference 1. The effects observed on workers are summarized below, to emphasize the need for personnel hygiene.

- Chloracne (moderate to severe skin irritation, with swelling, hardening, blackheads, pustules and pimples)
- Hyperpigmentation (skin discoloration)
- Hirsutism
- Eye irritation
- Muscular pain (legs, arms, back, breast)
- Decreased libido
- Fatigue
- Nervous irritability
- Intolerance to cold
- Destruction of nerve fibers and nerve sheaths

In addition, some effects on exposed test animals were observed. These may be considered possible effects on the human system, especially when the metabolism of the animal is similar to that of man. These effects include toxicity to embryos, birth defects, possible carcinogenicity, and even death. It should also be noted that the greatest hazard is to pregnant females and their fetuses, especially in the first third of the pregnancy period.

The need for personal cleanliness is pointed up by the methods of entry of TCDD into the body. These are:

- Through the mouth (ingestion)
- Through the skin (percutaneous)
- Through the lungs and eyes

Thus, eating, drinking, and smoking in working areas; wearing contaminated clothes; leaving liquids on the skin, failure to shower frequently and, especially, immediately after exposure; and breathing contaminated air must be avoided.

Discussions have been held with Col. Walter W. Melvin, Jr., M.D., USAF Environmental Health Laboratory, Kelly AFB, Texas, and Dr. V.K. Rowe, Corporate Offices, Dow Chemical Co., Midland, Michigan, concerning methods of personnel hygiene. They concur with the concepts of personal cleanliness, isolation of contaminated areas, and preservation of "clean" areas which are described herein.

Most procedures designed to protect personnel from hazards are a compromise between the ideal of complete avoidance of exposure and the reality of providing safe conditions and areas in which work can be done.

In the present case, good personal hygiene practices are of prime importance in preventing exposure of personnel to materials containing TCDD. Of equal importance is the establishment of "clean" areas, in which personnel can co-exist normally; the isolation of the hazard in areas where contamination is expected and can be dealt with; and the maintenance of an interface between the two areas which can be crossed while maintaining the integrity of the clean area and the safety of personnel therein.

It is anticipated that the first opportunity for exposure will come from spills and leaks in the system. The exposed liquids will evaporate, especially from hot decks and tankage areas below decks, and the very hot combustor room.

The liquids may be tracked over the decks and passageways, and may find their way into the eating and living quarters unless an inviolate interface is established between the two areas.

The basic requirements for effective personnel hygiene against TCDD-containing materials are:

- Protection of personnel for vapor and liquid contact in the contaminated areas by source control and protective gear
- Provision of disposable clothing and foot covers
- Provision of disposal facilities at the interface region between the contaminated and clean areas
- Provision for a shower, hand, face and eye-washing facilities at the interface region
- Provision of clean clothing and foot covering at the boundary of the clean area upon return to working areas
- Instruction in the use of the cleaning and protective equipment and in methods of personal cleansing
- Mandatory and enforced use of the above facilities and concepts.

Smoking, eating or drinking from containers or cups should be avoided in potentially contaminated areas. This also applies to personnel who have not showered or otherwise cleansed themselves after being in potentially contaminated areas.

The routes by which personnel move should be so arranged that entrance to the working area and exits from the working area are separate. Shoe covers which can be disposed of must be provided at entrances, and provision for their removal and disposal at exits must be made.

A monitoring system for ensuring that clean areas, such as the galley, mess room, living quarters, bridge, toilets and passageways, should be developed and put into effect on a firm basis. A schedule of inspection of the clean areas should be established, and the results of the monitoring made known to the ship's master.

Finally, all working personnel should be made aware of the need for good personal hygiene and of the consequences to themselves and others of poor personal cleanliness and poor housekeeping. A training program should be developed and personnel should be trained in personal hygiene practices. The effectiveness of the program will depend on the degree to which personnel accept the training, willingly put the principles to use, and cooperate in preventing exposures. Personnel who are unwilling or unable to accept and apply the personal hygiene procedures should be excluded from contact with and entry to the working area by direction of the ship's master.

6. SAFETY PROCEDURES AND MONITORING

The safety of all shipboard personnel will have top priority during the incineration of Herbicide Orange onboard the M/T Vulcanus. As a minimum, the following safety precautions are required as they apply before, during and after burn operations. These safety precautions are grouped by participating organizations to define and emphasize areas of responsibility.

M/T Vulcanus

1) All waste tank openings and viewing ports shall be closed. A closed system shall be maintained such that vapors do not escape into the atmosphere for the duration of the operation.

2) Any Herbicide Orange spills, leaks or residuals detected shall be immediately contained and decontaminated.

3) Measuring the tankage contents shall be with a closed gaging system. A schedule of tank content measurement and rate of depletion shall be established.

4) The cause of apparently random and often severe vibrations from the incinerators at frequent intervals during previous waste burns shall be identified. Steps to eliminate this condition shall be identified and implemented.

5) Fugitive Herbicide Orange emissions from the waste pumping room or any other source shall be eliminated.

6) An automatic shut-off device shall be in operation on both furnaces, set to turn off the flow of Herbicide Orange if the flame temperature drops below 1250°C.

7) The furnaces may be brought up to operating temperature at a rate consistent with ship's practice and experience, using fuel oil. When a flame temperature of 1280°C has been reached in the furnace (using correlated thermocouple or optical pyrometer measurements) the feed stock may be switched over to Herbicide Orange. The practice of converting to Herbicide Orange feed by putting furnaces on stream successively should be followed. The temperature of the furnace as read at the control panel should not be allowed to drop

more than 20°C at this time and must be restored to at least the original level of 1280°C before the next burner is changed over to Herbicide Orange.

8) Monitoring of the furnaces for temperature, and for completeness of combustion, shall be in effect during the changeover. The continuous record of temperature shall also be maintained during this time.

9) The operational controls and monitoring panels shall be manned at all times by a responsible individual to ensure the incinerators are operating within desired combustion parameters.

10) An automatic sealed monitoring device (black box) will be installed to record incineration activities and temperatures and camera to photograph the control panel every 15-30 minutes. In addition, a manual log will also be kept, including:

    a) Time, date
    b) "Black box" temperature
    c) Controller temperature reading
    d) Waste feed rates
    e) Switching of waste tanks
    f) Wind speed and direction
    g) Location

11) A device for addition of ammonia to make a visible plume shall be installed and operable.

12) The speed and direction of the M/T Vulcanus during waste incineration shall be controlled in such a manner that the incinerator plume does not contact any part of the ship at any time because of wind (eddies) or any other reason. The M/T Vulcanus shall stay under the main propulsion all the time so that plume impingement on the ship may be avoided by proper vectoring of the ship with respect to wind direction changes. Additionally, if the ship must assume a course and speed to stay in the burn area and if that course and speed result in undesirable plume conditions for safe operation, then the incinerators shall be temporarily shut down or revert to fuel oil until safe conditions can again be met.

13) The Vulcanus should demonstrate the ability to remain in constant 24-hour communication with the Johnston Island USAF On Scene Coordinator by voice and by code, using frequencies and channel appropriate to the area and to the conditions of transmission and reception. The requirement supplements but is not intended to supersede nor replace the existing

communication equipment. Daily communication with the Johnston Island USAF On Scene Coordinator shall be required reporting test progress and conditions. Emergency conditions shall be reported as soon as possible.

14) Personnel of the M/T Vulcanus shall give a briefing on ship safety procedures and regulations. This shall include, but not be limited to, the assignment of lifeboat seating positions and at least one lifeboat drill.

15) The M/T Vulcanus shall comply with all applicable U.S. Coast Guard rules and regulations governing a ship of this class and specification.

U.S. Air Force

1) Ambient air monitors shall be furnished to all members of the TRW sampling/monitoring crew. These monitoring units shall be analyzed at the Johnston Island Laboratory for 2,4-D, and 2,4,5-T. If TCDD analysis is required, this shall be done by Wright State University.

2) Appropriate first aid and medical supplies and trained medical personnel shall be available on Johnston Island to respond to emergency situations on board the M/T Vulcanus. Such facilities shall also be available to shipboard personnel while based on Johnston Island.

3) A plan shall be developed and available to cover emergency rescue or medical requirements of TRW and Vulcanus personnel during operations at sea. An Air Force representative shall brief all TRW personnel as well as key Vulcanus personnel (as determined by the ship's captain) regarding the provisions of this plan.

TRW, Inc.

1) The M/T Vulcanus crew and any other shipboard personnel boarding the M/T Vulcanus shall be briefed by USAF medical personnel and the Project Safety Director.

2) Monitoring of the incinerator stacks for CO/CO_2 concentrations shall be carried out by the TRW sampling/monitoring crew. The CO/CO_2 determinations shall be used to assure that the desired degree of combustion efficiency (99.9%) is achieved during the incineration.

3) Sampling of the incinerator stacks for the determination of 2,4-D, 2,4,5-T and TCDD emissions, if any, shall be carried out by the TRW sampling/monitoring crew. The 2,4-D and 2,4,5-T levels in the incinerator stacks shall be determined onboard the M/T Vulcanus by the TRW sampling/monitoring

crew with the use of a benzene sampling train and a gas chromatograph. The maximum allowable combined 2,4-D/2,4,5-T levels in the incinerator stacks shall be 130 mg/m^3.

4) **An onboard ambient air monitoring system shall be used by** the TRW sampling/monitoring crew to monitor the 2,4-D/2,4,5-T level in the galley, mess room and crews quarters, the combustion room, and the deck areas to assure that the atmosphere does not contain materials at or above a prohibited level of concentration. These measurements shall not be limited to only the **times when sampling is taking place.** Measurements indicating the presence of combined 2,4-D/2,4,5-T level above 2.0 mg/m^3 shall be immediately reported and steps shall be taken by the M/T Vulcanus personnel to correct the situation.

ATTACHMENT A

FIRST AID

The first aid instructions in the event of chemical poisoning, as given in J.B. Bailey and J.E. Swift "Pesticide Information and Safety Manual" (University of California, Division of Agricultural Sciences, July 1968), are reproduced in the next two pages. These first aid instructions are applicable to chemical poisoning by Herbicide Orange.

FIRST AID IN THE EVENT OF CHEMICAL POISONING

If You Are Along With the Victim...

FIRST — See that the victim is breathing; if not, give artificial respiration.

SECOND — Decontaminate him immediately i.e., wash him off thoroughly. Speed is essential!

THIRD — Call your physician.

NOTE: Do not substitute first aid for professional treatment. First aid is only to relieve the patient before medical help is reached.

If Another Person Is With You and the Victim...

Speed is essential; one person should begin first aid treatment while the other calls a physician.

The physician will give you instructions. He will very likely tell you to get the victim to the emergency room of a hospital. The equipment needed for proper treatment is there. Only if this is impossible should the physician be called to the site of the accident.

General

1. Give mouth-to-mouth artificial respiration if breathing has stopped or is labored.
2. Stop exposure to the poison and if poison is on skin cleanse the person, including hair and fingernails. If swallowed, induce vomiting.
3. Save the pesticide container and material in it if any remains; get readable label or name of chemical(s) for the physician. If the poison is not known, save a sample of the vomitus.

Specific

POISON ON SKIN

- Drench skin and clothing with water (shower, hose, faucet).
- Remove clothing.
- Cleanse skin and hair thoroughly with soap and water; rapidity in washing is most important in reducing extent of injury.
- Dry and wrap in blanket.

POISON IN EYE

- Hold eyelids open, wash eyes with gentle stream of clean running water immediately. Use copious amounts. Delay of a few seconds greatly increases extent of injury.
- Continue washing for 15 minutes or more.
- Do not use chemicals or drugs in wash water. They may increase the extent of injury.

INHALED POISONS (Dusts, Vapors, Gases)

- If victim is in enclosed space, do not go in after him without air-supplied respirator.
- Carry patient (do not let him walk) to fresh air immediately.
- Open all doors and windows, if any.
- Loosen all tight clothing.
- Apply artificial respiration if breathing has stopped or is irregular.
- Call a physician.
- Prevent chilling (wrap patient in blankets but don't overheat him).
- Keep patient as quiet as possible.
- If patient is convulsing, watch his breathing and protect him from falling and striking his head on the floor or wall. Keep his chin up so his air passage will remain free for breating.
- Do not give alcohol in any form.

SWALLOWED POISONS

- CALL A PHYSICIAN IMMEDIATELY
- DO NOT induce vomiting if:

  1) Patient is in a coma or unconscious.
  2) Patient is in convulsions
  3) Patient has swallowed petroleum products (that is, kerosene, gasoline, lighter fluid).
  4) Patient has swallowed a corrosive poison (strong acid or alkaline products); symptoms: severe pain, burning sensation in mouth and throat.

- If the patient can swallow after ingesting a corrosive poison, give the following substances by mouth. A corrosive substance is any material which in contact with living tissue will cause destruction of tissue by chemical action such as lye, acids, Lysol, etc.

  For acids: milk, water, or milk of magnesia (1 tablespoon to cup of water).

  For alkali: milk or water; for patients 1-5 years old, 1 to 2 cups; for patients 5 years and older, up to 1 quart.

IF POSSIBLE INDUCE VOMITING WHEN NON-CORROSIVE SUBSTANCE HAS BEEN SWALLOWED

- Give milk or water (for patient 1-5 years old — 1 to 2 cups; for patients over 5 years — up to 1 quart).
- Induce vomiting by placing the blunt end of a spoon not the handle, or your finger at the back of the patient's throat, or by use of this emetic — 2 tablespoons of salt in a glass of warm water.
- When retching and vomiting begin, place patient face down with head lowered, thus preventing vomitus from entering lungs and causing further damage. Do not let him lie on his back.
- Do not waste excessive time in inducing vomiting if the hospital is a long distance away. It is better to spend the time getting the patient to the hospital where drugs can be administered to induce vomiting and/or stomach pumps are available.
- Clean vomitus from person. Collect some in case physician needs it for chemical tests.

CHEMICAL BURNS OF SKIN

- Wash with large quantities of running water.
- Remove contaminated clothing.
- Immediately cover with loosely applied clean cloth, any kind will do, depending on the size of the area burned.
- Avoid use of ointments, greases, powders, and other drugs in first aid treatment of burns.
- Treat shock by keeping patient flat, keeping him warm, and reassuring him until arrival of physician.

APPENDIX B

TOXICOLOGICAL PROPERTIES OF 2,4-D, 2,4,5-T AND TCDD

TOXICOLOGICAL PROPERTIES OF 2,4-D, 2,4,5-T AND TCDD

The toxicological properties of 2,4-D, 2,4,5-T and TCDD, as compiled by the U.S. Air Force in the Report "Amendment to the Final Environmental Statement on the Disposition of Orange Herbicide by Incineration," October 1976, are included in the following pages.

4. TOXICOLOGICAL AND ECOLOGICAL CHARACTERISTICS OF CHLOROPHENOXY HERBICIDES PERTINENT TO POTENTIAL BIOLOGICAL EFFECTS OF N-BUTYL ESTERS OF 2,4-D AND 2,4,5-T:

There have been many scientific studies to determine the behavior of chlorophenoxy herbicides in plant and animal systems under varied environmental conditions. The following paragraphs are not meant to list all those studies. Rather, the purpose is to logically describe the known and probable behavior of Orange herbicide components in biological systems by utilizing the most current and relative information obtainable from the literature and from studies at EHL(K). It is important to note at the outset that in biological systems and aquatic systems the N-butyl esters (NBE) of 2,4-D and 2,4,5-T can hydrolyze. Thus, the behavior of the pure acids and their salts are also pertinent and will be discussed in the following paragraphs along with characteristics of ester forms. The differences in toxic effects produced by the various salts, amines and esters of 2,4-D and 2,4,5-T can often be explained on a pharmacokinetic basis in which the concentrations at the receptor sites in the organism depends on the absorption and distribution rates in relation to the rates of metabolism and excretion. The rate of absorption into plants or animals will be dependent upon various interrelated factors such as route of entry and rate of membrane transport. Specific membrane transport rate will depend upon the characteristics of the membrane in relation to the size, shape, polarity and lipid solubility of the particular herbicide molecule being considered in each cited study.

a. Behavior in Terrestrial Animals

(1) Metabolism and Excretion Kinetics: Most of the data derived from acute toxicity studies indicate that neither 2,4-D nor 2,4,5-T are particularly toxic. (Gleason *et al.*, 1969; Bjorklund and Erne, 1966). In the rat, the single dose, LD_{50} ranges from about 250-270 mg/kg depending on the forms of chemical administered (Christensen, 1971). Several workers have suggested that part of the reason for this lack of toxicity is that the excretion of the herbicides is very rapid in most mammals (Clark *et al.*, 1964; Khanna and Fang, 1966). Most studies indicate that animals possessing highly developed renal function will rapidly eliminate 2,4-D and 2,4,5-T by active tubular secretion. Cattle and rabbits, which normally actively metabolize compounds mostly by acetylation, excrete 2,4-D and 2,4,5-T in the urine mostly unchanged. Erne, (1966) found

that in the rat, rabbit, calf and chicken, 2,4-D and 2,4,5-T had a biological half-life varying from three to twelve hours and that urinary excretion was the most common route of elimination. Data exist to indicate that only very small amounts of 2,4-D are metabolized by the rabbit (Clark _et al_., 1964; Kahnna and Fang, 1966). Berndt and Koschier (1973) studied the _in vitro_ uptake of 2,4-D and 2,4,5-T by the renal cortical tissue of rabbits and rats. Renal cortical slices from both species accumulate 2,4-D and 2,4,5-T with greater uptake occurring in rabbit tissue. Nitrogen and various metabolic inhibitors reduced the uptake thus indicating that both of these organic acid herbicides are transported by the renal organic anion mechanism. Berndt and Koschier (1973) concluded that renal tubular transport by the organic anion mechanism may account for the relatively rapid disappearance of these compounds and this may account for their low toxicity.

(2) _Absorption and Distribution_: The most common route of accidental absorption of chlorophenoxy herbicide in terrestrial animals is via ingestion. This is especially true in herbivores. However, absorption of toxic doses via inhalation and cutaneous routes is possible, if uncommon. The literature indicates that gastric absorption of 2,4-D and 2,4,5-T and their amines and alkali salts occur readily as would be predicted from classical Henderson-Hasselbalch relationships. However, the gastro-intestinal absorption of 2,4-D in the form of an ester may be incomplete. Erne (1966) administered 2,4-D ester orally and found no detectable esters in the plasma. However, detection of low levels of 2,4-D in the plasma indicated that some hydrolysis of the ester had occurred. Erne (1966) in studies with rats, calves, chickens, and pigs found that the highest tissue levels of 2,4-D and 2,4,5-T were found in liver, kidney, lung and spleen, the levels sometimes exceeding the plasma level. In blood cells, 10-20% of the plasma level was found. Penetration of 2,4-D into adipose tissue and into the central nervous system was restricted, whereas a ready placental transfer was demonstrated in swine. The distribution pattern did not show any significant species or — in rats — sex differences. Klingman _et al_. (1966) measured ppb amounts of 2,4-D in the milk from cows grazing on pasture probably sprayed with esters of 2,4-D. However, these levels dropped to undetectable amounts (<1 ppb) on the third day after the pasture had been sprayed.

(3) Acute Toxicity: One of the essential prerequisites in the selection of a herbicide for defoliation programs is selective toxicity. Orange herbicide is characterized by a low order of toxicity to man and terrestrial animals. When properly applied, chlorophenoxy herbicides have presented very minimal hazards to animal life in target areas. The acute oral toxicity of Orange herbicide is summarized below. The data are expressed as LD_{50}s in units of mg of chemical per kg of body weight. This is the single oral dose which was lethal for 50% of the test species. Orange herbicide LD_{50}: rat 566, sheep 250 and cattle 250. The oral toxicities of 2,4-D and 2,4,5-T are quite similar to those of Orange herbicide (e.g., the acute oral LD_{50} of 2,4-D and 2,4,5-T in the rat are 620 and 480 mg/kg, respectively). Table B-1 and B-2 summarize the results of several acute toxicity studies with various salt, ester and amine forms of 2,4-D and 2,4,5-T.

(4) Chronic Toxicity: Because of the active secretion of chlorophenoxy herbicides, rather large amounts must be administered over a long period of time to produce symptoms of toxicity. Enormous amounts of Orange herbicide were applied to test plots at Eglin AFB without visible toxic effects or development of herbicide residues in the native animals in the test plots (Young, 1973). In one study, (Palmer and Radeleff, 1964) sheep were given 2 gm of the acid daily and sacrificed on the day following the final dose. Residues in the tissues were less than 1 ppm in all tissues and usually less than 0.05 ppm, which was the sensitivity of the analytical method. Mitchell and co-workers (1946) pastured sheep and cattle on treated foliage without harmful effects to the animals. They also fed a lactating cow 5.5 gm of 2,4-D daily for 106 days without producing poisoning. Palmer (1963) found that cattle were not harmed by 112 daily doses (administered 5 days each week) of 5 mg/kg of alkanolamine salt and that 44 daily doses of 200 mg/kg or 20 doses of 250 mg/kg were required to produce fatal poisoning. Palmer Radeleff (1964) reported that sheep were given 481 daily doses of 100 mg/kg doses of 2,4-D without producing poisoning. 2,4,5-T has not been investigated as thoroughly as 2,4-D, but the reaction of cattle and sheep to massive doses would indicate that absorption and excretion must follow a similar pattern. A study by Palmer and Radeleff (1964) showed that sheep required 369 doses of 100 mg/kg each to induce intoxication. The above results are summarized in Table B-3.

TABLE B-1. ACUTE TOXICITY OF 2,4-D DERIVATIVES TO TERRESTRIAL ANIMALS

Derivative	Animal	Dose	Effect	Reference
Alkanolamine	Chick	380-765 mg/kg	LD_{50}	Rowe, et al. (1954)
Isopropyl ester	Rat	700 mg/kg	LD_{50}	Rowe, et al. (1954)
Isopropyl ester	Chicks	1420 mg/kg	LD_{50}	Rowe, et al. (1954)
Isopropyl ester	Guinea pig	550 mg/kg	LD_{50}	Rowe, et al. (9154)
Butyl ester	Rat	620 mg/kg	LD_{50}	Rowe, et al. (1954)
Butyl ester	Guinea pig	848 mg/kg	LD_{50}	Rowe, et al. (1954)
Butyl ester	Chicks	2000 mg/kg	LD_{50}	Rowe, et al. (1954)
PGBE	Rat	570 mg/kg	LD_{50}	Rowe, et al. (1954)
Acid	Dog	100 mg/kg	LD_{50}	Rowe, et al. (1954)
Acid	Chick	541 mg/kg	LD_{50}	Rowe, et al. (1954)
Triethanolamine	Swine	50 mg/kg	No effect	Bjorklund & Erne (1966)
Triethanolamine	Swine	500 mg/kg	Lethal	Bjorklund & Erne (1966)
Butyl ester	Swine	100 mg/kg	No effect	Bjorklund & Erne (1966)
Triethanolamine	Chicken	300 mg/kg	No effect	Bjorklund & Erne (1966)
Butyl ester	Rat	620 mg/kg	LD_{50}	Edson et al. (1964)
Isopropyl ester	Rat	700 mg/kg	LD_{50}	Hayes, (1963)
Unspecified amine	Mallard duck	2000 mg/kg	LD_{50}	Tucker & Crabtree (1970)
Acid	Pheasant	472 mg/kg	LD_{50}	Tucker & Crabtree (1970)
Acid	Mule deer	400-800 mg/kg	LD_{50}	Tucker & Crabtree (1970)

TABLE B-2. ACUTE TOXICITY OF 2,4,5-T DERIVATIVES TO TERRESTRIAL ANIMALS

Derivative	Animal	Dose	Effect	Reference
Acid	Rat	500 mg/kg	LD_{50}	Rowe & Hymas (1954)
Isopropyl ester	Mice	551 mg/kg	LD_{50}	Rowe & Hymas (1954)
Butyl ester	Mice	940 mg/kg	LD_{50}	Rowe & Hymas (1954)
Amyl ester	Rat	750 mg/kg	LD_{50}	Rowe & Hymas (1954)

b. Behavior in Humans: Gehring et al., (1973) studied the effects of 2,4,5-T at a dose level of 5 mg/kg ingested directly in a slurry of milk. Analytical grade 2,4,5-T having a purity of greater than 99% and containing less than the detectable level 0.05 ppm, of TCDD was used. Complete medical histories, physical and laboratory studies were accomplished before and repeated after the study. It was found that the clearances of 2,4,5-T and the excretion from the body were by first-order rate processes with half-lives of 23.10 and 23.06 hours, respectively. Essentially all of the ingested 2,4,5-T was absorbed into the body and was excreted unchanged in the urine. Following ingestion, 65% of the 2,4,5-T remained in the plasma where 98% was reversibly bound to the plasma proteins. "No untoward effects associated with the ingestion of 5 mg/kg, 2,4,5-T were detected in any of the subjects." (Gehring et al., 1973) A metallic taste lasting 1-2 hours following ingestion was reported by most of the subjects. It was also concluded that essentially all of the ingested 2,4,5-T was absorbed and then eliminated unchanged in the urine.

c. Behavior in Aquatic Systems and Aquatic Animals

(1) Metabolism and Distribution

(a) General Comparisons: The behavior of the chlorophenoxy herbicides in non-mammalian aquatic animals is quite different than the behavior described for terrestrial mammals and birds. The herbicides have a greater toxic potential for aquatic animals. First, the route of entry is different in

TABLE B-3. CHRONIC TOXICITY OF 2,4-D AND 2,4,5-T DERIVATIVES TO TERRESTRIAL ANIMALS

Chronic Toxicity of 2,4-D					
Derivative	Animal	Dose	Duration	Effect	Reference
Triethanolamine	Swine	50/mg/kg/day	3 doses	None	Bjorklund & Erne (1966)
Triethanolamine	Swine	50/mg/kg/day	8-10 doses	Minor transient effects	Bjorklund & Erne (1966)
Butyl ester	Swine	50/mg/kg/day	<5 doses	None	Bjorklund & Erne (1966)
Triethanolamine	Swine	500 ppm in feed	1 month	Some locomotory disturbance, depressed growth rate, no gross pathology	Bjorklund & Erne (1966)
Triethanolamine	Rats	1000 ppm in water	10 mos.	Depressed growth rate, no gross pathology	Bjorklund & Erne (1966)
Triethanolamine	Chicken	1000 ppm in water	Daily from hatching through first 2 mos. of egg production	Egg size normal, production reduced 30%	Bjorklund & Erne (1966)
Alkanolamine	Sheep	100/mg/kg/day	481 days	No effect	Palmer & Radeleff (1964)
Alkanolamine	Cattle	50/mg/kg/day	112 days	No effect	Palmer & Radeleff (1964)

TABLE B-3. CHRONIC TOXICITY OF 2,4-D AND 2,4,5-T DERIVATIVES TO TERRESTRIAL ANIMALS (Continued)

Derivative	Animal	Dose	Duration	Effect	Reference
PGBE ester	Sheep	100 mg/kg/day	481 days	No effect	Palmer & Radeleff (1964)
Ethylhexyl ester	Cattle	250/mg/kg/day	14 days	Ill in 3 days, survive and recover from 9 doses. 14 doses lethal	Hunt, et al. (1970)
Ethylhexyl ester	Sheep	250/mg/kg/day	17 days	Ill in 3 days, 17 doses lethal	Hunt, et al. (1970)
Ethylhexyl ester	Sheep & Cattle	100/mg/kg/day	10 days	None to minor effects	Hunt, et al. (1970)
Not specified	Dog	500 ppm in feed	2 years	None	House, et al. (1967)
Not specified	Rat	1250 ppm in feed	2 years	No effects on growth, survival hermatology or tumor incidence	House, et al. (1967)
Not specified	Rat	500 ppm in feed	2 years	No effects in reproduction studies	House, et al. (1967)
Alkanolamine	Chicken	100 mg/kg/day	10 days	No effect on weight gain	Palmer & Radeleff (1969)
PGBE ester	Chicken	50 mg/kg/day	10 days	No effect on weight gain	Palmer & Radeleff (1969)

TABLE B-3. CHRONIC TOXICITY OF 2,4-D AND 2,4,5-T DERIVATIVES TO TERRESTRIAL ANIMALS (Continued)

Derivative	Animal	Dose	Duration	Effect	Reference
PGBE ester	Cattle	100 mg/kg/day	10 days	No effect	Palmer & Radeleff (1969)
Acid	Mule deer	80 and 240 mg/kg/day	30 days	Minor symptoms no weight loss	Tucker and Crabtree (1970)

Chronic Toxicity of 2,4,5-T

Formulation	Organism	Dose	Duration	Effect	Reference
Not specified	Dog	10 mg/kg/day	5 days per wk. for 90 days	Minor weight loss, no other effects	Drill & Hiratzka (1953)
Not specified	Dog	20 mg/kg/day	5 days per wk. for 90 days	Lethal between 11 and 75 days	Drill & Hiratzka (1953)
PGBE ester	Cattle	100 mg/kg/day	10 days	None	Palmer & Radeleff (1969)
PGBE ester	Sheep	50 mg/kg/day	10 days	None	Palmer & Radeleff (1969)
PGBE ester	Sheep	100 mg/kg/day	369 days	(dosed by capsule) Ill at 367 doses, lethal at 369	Palmer & Radeleff (1969)
PGBE ester	Chicken	100 mg/kg/day	10 days	No effect on weight gain	Palmer & Radeleff (1969)

TABLE B-3. CHRONIC TOXICITY OF 2,4-D AND 2,4,5-T DERIVATIVES TO TERRESTRIAL ANIMALS (Continued)

Formulation	Organism	Dose	Duration	Effect	Reference
Triethylamine	Sheep	100 mg/kg/day	481 days	No effect	Palmer & Radeleff (1964)
Not specified	Mice	21 mg/kg/day 600 ppm in diet.	4 weeks 18 months	No mortality	Innes, et al.

From Oregon E.I.S. (EIS-OR, 1973)

most instances. The aquatic animal absorbs the herbicide which is distributed throughout his total environment (absorption is mainly via gills in fish). Then, the differences in renal function must be considered. Generally, nonmammlian aquatic animals do not have highly developed kidneys. Thus, once the herbicide is in the aquatic animal's body, some metabolic changes must occur in the molecule to make it more polar if it is to be excreted. Toxicity testing is also necessarily different with aquatic animals. Usually, aquatic animals are placed in a concentration of the toxicant to gradually absorb the material at a rate depending on the animal's physiology and the behavior of the toxicant in the particular water conditions. Therefore, the actual dose to each animal is not known in most studies with aquatic animals. In contrast, toxicity studies with terrestrial animals usually allow calculation of a known dose per unit weight of each animal. Thus, toxicities are often reported as "LD_{xx}" (Lethal Dose) for terrestrial animals and "LC_{xx}" (Lethal Concentration) for aquatic animals.

(b) Metabolism in Fish: Donald P. Shultz (Fish-Pesticide Research Laboratory, Bureau of Sport Fisheries and Wildlife, 1973) studied the uptake, distribution, and dissipation of ^{14}C-label dimethyl amine salt of 2,4-D (DMA-2,4-D). Three species of fish were exposed to 0.5, 1.0 or 2.0 mg/l concentrations of herbicide for up to 84 days exposure period. No mortalities occurred, nor were adverse biological effects observed at these exposure levels. The highest radioactive residue found in muscle tissue occurred in Bluegills exposed to 2.0 mg/l for 84 days (1.065 mg/kg). However, gas-liquid chromatography indicated that over 90% of the radioactive residues consisted of metabolites of 2,4-D. The major metabolite in the fish was found to be 2,4-D glucuronic acid conjugate. Current investigations have found at least six metabolites of 2,4-D in fish. Thus, in contrast to many of the organochlorine pesticides which undergo biomagnification through the food chain, DMA-2,4-D is metabolized in fish without accumulation of the parent compound.

(2) Behavior in Aquatic Systems

(a) Solubility Limits and Rates Vs. Hydrolysis Rates: The esters of 2,4-D or 2,4,5-T found in Orange herbicide have a very limited solubility in water. Because of this very low solubility, the actual concentrations of esters produced in a body of water by accidental contamination would likely be much less than the "expected value" calculated from the volumes involved. The USAF EHL(K) is in the process of studying the behavior of Orange herbicide in aquatic systems especially sea water. In one study using artificial sea water*, Orange herbicide was mixed into the water in an amount equal to 150 mg/l. Had all components gone right into solution, by computation, ester concentrations would have been 64 mg/l (2,4-D NBE) and 61 mg/l (2,4,5-T NBE). The actual, measured concentrations were 2 mg/l (2,4-D NBE) and 1.8 mg/l (2,4,5-T NBE) immediately after mixing. These increased to 18 and 22 mg/l of 2,4-D NBE and 2,4,5-T NBE, respectively, at 24 hours and then started a rapid decline to 7.5 and 9.5 mg/l at 48 hours after mixing. The rate of disappearance of the ester of 2,4-D was fairly rapid and was assumed to be mainly a result of hydrolysis. The half-life of the ester was 15 hours. The addition of natural biota such as bacteria, algae and fish would be expected to produce an even faster disappearance of 2,4-D NBE. Evidence that this occurs was observed in studies EHL(K) is conducting with marine animals at the National Marine Fisheries Laboratory in Port Aransas, Texas. In one of these studies, shrimp were exposed in five different concentrations of 2,4-D NBE and natural sea water. The average half-life of the ester in the five concentrations was 5 hours. This was 1/3 of the half-life observed in the situation where no biological systems existed.

(b) Circulation of Water in Relation to Availability of Herbicide for Absorption: Some of the toxicity studies completed so far indicate the complexity of trying to predict the ecological results of a planned or accidental contamination of a body of water with phenoxy herbicides. At EHL(K), Orange herbicide was mixed in a fish tank at a concentration that would theoretically produce a 200 $\text{ppm}_{v/v}$ concentration if such a high concentration were possible. Most of the herbicide rapidly sank to the bottom of the tank after mixing. Fathead minnows placed in the tank showed no ill effects during two weeks of exposure. Yet in a toxicity study under the same conditions but with continuous agitation of the water by aeration, all of the fish died in a "20 ppm concentration" of Orange herbicide water in 24 hours. Subsequent studies revealed that some circulation of the water was essential if a dose-related response was to be established in toxicity studies with the N-butyl esters of 2,4-D and 2,4,5-T. Thus, the actual effect seen in nature might well depend on a factor such as the degree of mixing in the affected body of water.

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*Instant Ocean Aquarium Systems, Inc., East Lake, Ohio.

(c) Importance of Hydrolysis: It is important that when the esters of 2,4-D and 2,4,5-T hydrolyze, their toxicity to aquatic animals is decreased by almost a factor of 10 (paragraph (3)(b) below). In the static situation described in the paragraph above (no aeration), the rate of hydrolysis was probably faster than the rate that the ester went into solution so that lethal concentrations were never attained. Toxicity studies with freshwater and saltwater animals at EHL(K) have been the so-called "Static Bioassay" in which no attempt is made to maintain a constant concentration of the herbicide ester in each test chamber. "Concentrations" are theoretical and based on volumes of herbicide and water mixed together rather than from analysis of water to quantitate the herbicide. Most studies reported from literature are of the same type. The toxicity tests at EHL(K) revealed that in both freshwater and saltwater, most of the test organisms had responded at twelve hours of exposure. There was rarely any increase in mortality past 24 hours.

(d) Other Factors Affecting Actual Concentrations: Many other factors can influence the concentration of N-butyl esters of 2,4-D and 2,4,5-T in a body of water. In studies where large amounts of Orange herbicide were placed in water, the globules of the herbicide appeared to become coated with an opaque material that may have inhibited the ester from going into solution. Cope (1970) treated ponds with 0.5 ppm to 10 ppm propylene glycol butyl ether ester (PGBE) of 2,4-D. He was able to measure residues of herbicide absorbed or adsorbed in vegetation and bottom sediment for 6 weeks after treatment in the 10 ppm treated pond. Crosby (1966) reported that 2,4-D decomposes rapidly in the presence of water and ultraviolet light.

(3) Toxicity

(a) Factors Affecting Toxicity: The toxicity of the chlorophenoxy herbicides to aquatic animals varies considerably with many factors such as water chemistry variables, temperature, and the particular salt, ester or amine form of the herbicide considered. Species susceptibility varies greatly. For example, the 96-hour TL_{50}* for fathead minnows exposed to DMA-2,4-D was found to be 335 mg/l. Yet, for bluegills and channel catfish the TL_{50} values were 177 and 193 respectively. A temperature increase from 17°C to 20°C increased the relative toxicity to the catfish from TL_{50} of 193 mg/l to 125 mg/l (Schultz, 1973).

(b) Toxicity Comparisons by EHL(K): The USAF EHL(K) (1974), performed static toxicity studies with Orange herbicide. Also, toxicity studies were performed using each individual N-butyl ester of 2,4-D and 2,4,5-T. Freshwater bioassays using the fathead minnow (*Pimephales promelas*) resulted in a 48 hr LC_{50} of 3.4 ppm for Orange herbicide containing 14 ppm TCDD. The 48 hr LC_{50}s for esters of 2,4-D and 2,4,5-T were 2.8 ppm and 5 ppm respectively. The 48 hr LC_{50} for 2,4-D in the minnows was 270 ppm. The 2,4,5-T 48 hr LC_{50} concentration was 333 ppm. Note that the toxicity of ester formulations were considerably more toxic than the respective acid. Also, EHL(K) found the N-butyl ester of 2,4-D to be more toxic than the N-butyl ester of 2,4,5-T. In saltwater studies by EHL(K), the 48 hr LC_{50}* values in the shrimp (*Penaeus sp.*) were 5.6 ppm for 2,4-D NBE and 33 ppm for 2,4,5-T NBE. Oysters (*Crassostrea virginica*) were exposed to "potential concentrations" of 2,4-D NBE ranging from 0.5 ppm to 85 ppm. The only acute effect observed was the death of one of the oyster (10%) in the highest concentration at 48 hours.

(c) Other Animals and Other Effects: Many other aquatic animals besides fish can be affected by phenoxy herbicides. Saunders (1971) studied the effects of the propylene glycol butyl ether ester (PGBE) of 2,4-D on six freshwater crusteceans. He found the following 48 hr TL_{50}* values: Daphnia magna = 0.10 ppm, seed shrimp = 0.32 ppm, scud = 2.6 ppm, sowbug = 2.2 ppm, glass shrimp = 2.7 ppm, and crayfish had an unknown value larger than 100 ppm. Cope (1970) studied the chronic effects of PGBE ester of 2,4-D on the bluegills. Survivors of ponds treated with high concentrations (10 and 5 ppm) had a 2 week delay in spawning. For pathologic lesions, high-treatment fish had earlier and more severe effects than did low-treatment fish. The pathology involved the liver, vascular system and brain. Remarkably, growth of the fish was faster in the ponds receiving the high-treatment than in the lower-treatment ponds. Tables B-4 and B-5 were extracted from a U.S. Forest Service Environmental Impact Statement (EIS-OR, 1973). The tables indicate the effects of herbicides on other aquatic species and point out some toxic effects that can be measured other than death of the organisms.

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*TL_{50} and LC_{50} (Tolerance Limit and Lethal Concentration) are concentration values statistically derived from the establishment of a dose-related response of experimental organisms to a toxicant. The LC is based on a measured response of death only. the TL is based on a count of unaffected organisms. The subscript number for both indicates the percent response expected for the calculated concentration. Therefore, in most cases, the TL_{50} = LC_{50} or the concentration in which 50% death is expected. Note that a more toxic chemical has a smaller LC_{50}.

d. Behavior in Plants

(1) Distribution and Metabolism: Orange herbicide is a systematic herbicide that affects plants by a hormonal type of action usually described as "auxin-like" or "auxin-type." Auxins are any of a group of substances which promote plant growth by cell elongation, bring about root formation, or cause bud inhibition or other effects. 2,4-D and 2,4,5-T are compounds of this type. When applied to leaves of a plant, chlorophenoxy herbicides are absorbed through the cuticle into the plant system. The N-butyl ester forms of 2,4-D and 2,4,5-T found in Orange herbicide are usually more effective than more polar forms because of better absorption into the plant. This is also demonstrated in Yamaguchi's work (1965) in which he found that 2,4-D moves into plant leaves better from acidic solutions than from alkaline solutions. Approximately ten times as much 2,4-D was absorbed from a medium having pH 3 than one with pH 11. 2,4-D has a pK_a of 2.8 and would be highly disassociated at pH 11. Once the herbicide is in the plant it is translocated to areas where food is being stored as in rapidly growing new roots and shoots. The chlorophenoxy herbicides can be stored in certain cells of the plant. Also, metabolism occurs through degradation of the acetic acid side chain, hydroxylation of the aromatic ring, or conjugation.

(2) Toxicity: Once in the plant, herbicides act by interfering with the photosynthetic, respiratory, and other plant processes causing the plant to lose its leaves and ultimately die. Plant susceptibility to sublethal exposures of 2,4-D is markedly influenced by the growth condition of the plant and by environmental factors. Since most of the injury is expressed by growth response, the plant must be growing in order to show injury. In

TABLE B-4. ACUTE EFFECTS OF 2,4-D DERIVATIVES UPON AQUATIC ANIMALS

Derivative	Animal	Concentration	Effect	Reference
Isooctyl esters (From 3 manufacturers)	Bluegill	10-31 ppm	48 TLm	Hughes & Davis (1963)
PGBE ester	Bluegill	17 ppm	48 TLm	Hughes & Davis (1963)
Butoxyethanol ester	Bluegill	1.4 ppm	48 TLm	Hughes & Davis (1963)
PGBE ester	Shrimp	1 ppm (48 hrs)	20% mortality or paralysis	Butler (1965)
PGBE ester	Fish (saltwater)	0.32 ppm	48 hr TLm	Butler (1965)
Alkanolamine Salt	Bluegill	435-840 ppm	48 hr LC_{50}	Lawrence (1966)
Dimethylamine Salt	Bluegill	166-458 ppm	48 hr LC_{50}	Lawrence (1966)
Isooctyl ester	Bluegill	8.8-59.7 ppm	48 hr LC_{50}	Lawrence (1966)
Dimethylamine Salt	Fathead Minnow	10 ppm	96 hr LC_{50}	Lawrence (1966)
Acetamide	Fathead Minnow	5 ppm	96 hr LC_{50}	Lawrence (1966)
Oil soluble amine salt	Bluegill, Fathead Minnow	2 ppm	4 mo. LC_{10}	Lawrence (1966)
PGBE Ester*	Bluegill, Fathead Minnow	2 ppm	4 mo. LC_{10}	Lawrence (1966)
Butoxyethyl ester	Bluegill & Fathead	2 ppm	72 hr LC_{50}	Lawrence (1966)
Butyl and Isopropyl esters, mixed	Bluegill	1.5-1.7 ppm	48 hr LC_{50}	Lawrence (1966)
N,N-Dimethyl cocoamine salt	Bluegill	1.5 ppm	48 hr LC_{50}	Lawrence (1966)
Ethyl ester	Bluegill	1.4 ppm	48 hr LC_{50}	Lawrence (1966)
Butyl Ester	Bluegill	1.3 ppm	48 hr LC_{50}	Lawrence (1966)
Isopropyl ester	Bluegill	1.1 ppm	48 hr LC_{50}	Lawrence (1966)

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*Propylene Glycol Butyl Ether

TABLE B-5. NON-LETHAL EFFECTS OF 2,4-D DERIVATIVES UPON AQUATIC ANIMALS

Derivative	Animal	Dose	Effect	Reference
Butoxyethanol ester	Oyster	3.75 ppm (96 hrs)	50% decrease in shell growth	Butler (1965)
Butoxyethanol ester	Shrimp	1 ppm (48 hrs)	No effect	Butler (1965)
Butoxyethanol ester	Fish (saltwater)	5 ppm	48 hr. TLm	Butler (1965)
Butoxyethanol ester	Phyto-plankton	1 ppm	16% decrease in CO_2 fixation	Butler (1965)
Dimethylamine	Oyster	2 ppm (96 hrs)	No effect on shell growth	Butler (1965)
Dimethylamine	Shrimp	2 ppm (48 hrs)	10% mortality or paralysis	Butler (1965)
Dimethylamine	Fish (saltwater)	15 ppm (48 hrs)	No effect	Butler (1965)
Dimethylamine	Phyto-plankton	1 ppm (4 hrs)	No effect on CO_2 fixation	Butler (1965)
Ethylhexyl ester	Oyster	5 ppm (96 hrs)	38% decrease in shell growth	Butler (1965)
Ethylhexyl ester	Shrimp	2 ppm (48 hrs)	10% mortality or paralysis	Butler (1965)
Ethylhexyl ester	Fish (saltwater)	10 ppm (48 hrs)	No effect	Butler (1965)
Ethylhexyl ester	Phyto-plankton	1 ppm (4 hrs)	49% decrease in CO_2 fixation	Butler (1965)
PGBE 1/ ester	Oyster	1 ppm (96 hrs)	39% decrease in shell growth	Butler (1965)
PGBE 1/ ester	Shrimp	1 ppm (48 hrs)	No effect	Butler (1965)
PGBE 1/ ester	Fish (saltwater)	4.5 ppm	48 hr TLm	Butler (1965)

1/ PGBE is propylene glycol butyl ether.

addition, plants in shaded areas respond more slowly than those exposed to direct sunlight. Because of these various factors which affect plant response to the 2,4-D type herbicide, differences in lists showing plant susceptibility should be expected. Orange herbicide is effective on a wide variety of woody and broadleaf plant species. Other lower plant forms can also be affected by auxin-type herbicides. Even unicellular algae exhibit toxic effects or die when exposed to 2,4-D or 2,4,5-T (Walsh, 1972). However, much higher doses of the herbicides are required than for plants with a more complex structure.

(3) Herbicides as Air Pollutants: Although herbicides have long been accepted as environmental pollutants which affect sensitive vegetation, the air pollution aspects of volatile herbicides have not been widely explored. However, there is growing evidence that some 2,4-D compounds may be present in the ambient atmosphere in some parts of the United States at levels sufficient to cause adverse growth effects on sensitive vegetation. During 1962 through 1964, Vernetti and Freed measured 2,4-D concentrations in air samples taken in an agricultural area of eastern Oregon. Concurrently, they surveyed for auxin-like plant damage in the areas where the air samples were taken. In the spring of 1962, measured concentrations of the isopropyl ester of 2,4-D in the air ranged from 0.015 ppm to 0.64 ppm. This was during the time of year when the huge wheat fields of the area were being treated for weeds by aerial application of the isopropyl ester. Plant damage to tomato crops appeared to coincide with periods of highest measured concentrations of the isopropyl ester. Other plants, especially locust trees, also showed growth regulator symptoms. Legislation in the state curtailed the use of the isopropyl ester and decidedly reduced the contamination and resulting plant damage. Laboratory studies by Vernetti and Freed indicated that 0.015 ppm would be the threshold concentration of isopropyl ester that tomato plants could be exposed to and still survive under the conditions of the experiment. Volatility studies by the same workers demonstrated that the isopropyl ester was three times more volatile than the butyl ester. In fact, complex analyses of the air samples ruled out butyl and other esters of 2,4-D as principal contaminants.

(4) Relative Species Sensitivity: Different researchers vary in their results of relative plant sensitivity to phenoxy herbicides. From field observations, grapevines and box elder appear to be among the most sensitive

since they respond to 2,4-D air pollution when other plants showed no evidence of injury. Injury to grapevines may result from exposure to levels in the ppb range. Other workers report tomato plant damage in the ppt range. Walsh (1972) reports a 50% reduction in growth of unicellur marine algae exposed to phenoxy herbicide concentrations of 50 to 300 ppm. Other relative sensitivities are indicated in Table B-6.

5. TOXICOLOGICAL CHARACTERISTICS OF TCDD: The word teratology has rather recently become quite familiar to biologists, chemists and certain other persons working in various scientific disciplines. It was applied to 2,4,5-T when studies by Bionetics Research Laboratory, Division of Litton Industries, Bethseda MD in 1969-70 implied that 2,4,5-T was teratogenic in mice and rats (Courtney _et al_., 1970). Subsequently, studies revealed that a toxic contaminant was responsible for the findings originally attributed to 2,4,5-T. The sample of 2,4,5-T employed in the Bionetics study contained 27 ±8 ppm TCDD. Some studies have shown that oral administration of 2,4,5-T containing <1 ppm TCDD produces no teratogenic effects on rats, rabbits, mice and other species.

a. _Toxicity to Animals_: TCDD was found to be the most toxic chlorodibenzo-p-dioxin studied. It was found to have LD_{50}s in the μg/kg range for several species of animals and was acnegenic, highly embryotoxic and positive for the chick edema factor. "The no-effect dose levels for embryotoxicity and chick edema were 0.03 to 0.1 μg/kg/day respectively" (Schwetz _et al_., 1973).

(1) _Acute Toxicity_: Studies performed on TCDD by the Biochemical Research Laboratory, Dow Chemical Co., can be summarized as follows with the data presented as the LD_{50} in μg/kg of body weight for several species: rats 20-40; mice, males >64, females 130; guinea pig 0.6-2.0; rabbits ≈30; dogs >30 (Rowe _et al_., n.d.). The signs of intoxication are characterized by a chronic illness and liver damage. Half of the deaths occur more than two weeks after treatment while some animals died after 48 hours. Excretion is primarily by way of feces and is very slow. The highest concentrations are found in the liver and fat with a smaller amount being found in the testes. The LD_{50} for the rabbit is about the same whether administered intraperitoneally or applied to the skin. In the eye it does not cause corneal injury but does produce thickening of the lids. It does cause severe chloracne when applied to the ears of rabbits in μg quantities.

TABLE B-6. SENSITIVITY OF SELECTED PLANTS TO 2,4-DICHLOROPHENOXYACETIC ACID*

Sensitive

Apple
Malus, sp.

Birch
Betula, sp.

Boxelder
Acer negundo, L.

Dogwood
Cornus, sp.

Elderberry
Sambucus, sp.

Forsythia
Forsythia, sp.

Grape
Vitis, sp.

Hickory
Carya, sp.

Lambs-quarters
Chenopodium album, L.

Linden
Tilia, sp.

London plane tree
Platanus accrifolia (Ait.) Willd.

Maple, Norway
Acer platanoides, L.

Oak, black
Quercus velutina, Lam.

Sorrell
Rumex, sp.

Sumac
Rhus, sp.

Tobacco
Nicotiana, sp.

Tomato
Lycopersicon esculentum, Mill.

Treeofheaven
Ailanthus altissima, Mill.

Wisteria
Wisteria, sp.

Yellow wood
Cladrastis lutea, Kock

Zinnia
Zinnia, sp.

Intermediate

Aster, wild
Aster, sp.

Cedar Cherry
Prunus, sp.

Cherry, choke
Prunus virginiana, L.

Corn
Zea mays, L.

Mulberry
Morus, sp.

Oak, pin
Quercus palustris, L.

Oak, red
Quercus palustris, L.

Peach
Prunus persica, Sieb. & Zucc.

Ragweed, giant
Ambrosia trifida, L.

Rhododendron
Rhododendron, sp.

Rose
Rosa, sp.

Spruce, Colorado blue
Picea pungens, Englm.

TABLE B-6. SENSITIVITY OF SELECTED PLANTS TO 2,4-DICHLOROPHENOXYACETIC ACID* (Continued)

Gladiolus *Gladiolus*, sp.	Potato *Solanum tuberosum*, L.	Sweetgum *Liquidambar styraciflua*, L.
Hemlock *Tsuga*, sp.	Privet *Ligustrum*, sp.	Yew *Taxus*, sp.
	Resistant	
Ash *Fraxinus*, sp.	Eggplant *Solanum melongena*, L.	Rhubarb *Rheum rhaponticum*, L.
Bean, bush *Phaseolus vulgaris*, L.	Pear *Pyrus communis*, L.	Sorghum *Sorghum vulgare*, Pers.
Cabbage *Brassica oleracea*, L.	Peony *Paconia*, sp.	

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*From Air Pollution Control Association Report No. 1

(2) Toxic Effects on the Fetus

(a) Hamsters: Commercial samples of 2,4,5-T were shown by Collins and Williams (1971) to be feticidal and teratogenic in the golden Syrian hamster. Dose levels of 2,4,5-T ranged from 20 to 100 mg/kg/day while TCDD content varied from 0.1 to 45 ppm. Doses of 100 mg/kg/day of 2,4,5-T approach levels causing maternal mortality.

(b) Rats: TCDD is highly embryotoxic in the rat. No effect was seen at a dose level of 0.03 μg/kg/day but at the 0.125 μg/kg/day dose level there was a significant incidence of fetuses with intestinal hemorrhage; fetal deaths and resorptions increased. Delayed skeletal maturation was seen. At 2 μg/kg/day there were few viable fetuses and the survivors had a high incidence of anomalies. At 8 μg/kg/day there was severe maternal toxicity and there were no viable fetuses. King et al. (1971) studied the effect of 2,4,5-T and 2,4-D administered by gavage and an intrauterine technique using Sprague-Dawley rats as the test species. "Purified" and "technical" grade 2,4,5-T were applied to Millipore® filters that were then placed on the amniotic sac of the embryo. "Purified" 2,4,5-T intrauterinely applied to 93 embryos on any one day of gestation from day 12 to 16 at a dose range of 50 to 120 μg per embryo resulted in no cleft palates. Substituting the technical for purified grade and using the same technique on 118 embryos resulted in two cleft palates. Oral administration of 2,4-D and 2,4,5-T at a total dose range of 60 to 120 mg/kg to 245 rats yielded 2,231 fetuses, nine of which had cleft palates. Again, these are high dose levels.

b. Industrial Exposure: Dow Chemical Co. prepared an extensive health inventory of 126 manufacturing personnel in an effort to identify harmful effects of inhaled 2,4,5-T. The inhalation rate of the agent was estimated to be from 1.6 to 8.1 mg/day/worker, depending on work assignment, for periods of up to three years. The survey indicates that no illness was associated with 2,4,5-T intake. In plants where 2,4,5-T contained a high proportion of TCDD, Bleiberg et al. (1964) found 18% of the exposed employees suffered from moderate to severe chloracne, the intensity of which correlated significantly with the presence of hyperpigmentation, hirsutism and eye irritation. In the late 1940's a pressure overload resulted in the accidental rupture of a vessel containing the sodium salt of 2,4,5-trichlorophenol, a precursor of 2,4,5-T. During the following months, 228 persons developed chloracne, not only plant employees, but members of their families including wives and children. In workers more intensively exposed as a result of the accident, chloracne appeared about two weeks followed by moderate to severe pain in the skeletal muscles of the legs, arms, back and breath, decreased libido and intolerance to cold. Comedones appeared in areas of adult hair which is not typical of juvenile acne. There were pustules on the face, neck, abdomen, back and scrotum. Serum lipids, prothrombin time and glucuronates were all elevated. Biopsy of peripheral nerves revealed destruction of myelin sheaths and in some instances nerve fibers. Hyperpigmentation, fatigue and marked nervous irritability appeared. Over a period of several months, all of the symptoms and findings, except the scars of acne, returned to normal after removal from exposure. Cases in the families of the workers probably resulted from contaminated clothing and poor personal hygiene. The causative agent was not identified at the time. However, in the light of current knowledge, it was almost certainly a polychlorinated dibenzodioxin and possibly TCDD (Suskind, 1973).

c. Evaluation of Toxicological Testing

(1) Requirement for Establishing Dose-Related Response: Insistence on administering a "maximum tolerated dose" may be terribly misleading if this is the only dose tested, as in the Bionetics study (Innes, et al., 1969). There is no justification for abrogating the need to establish a dose-response relationship, which is fundamental to all toxicological experimentation. The route of administration is all important in tests for teratogenesis. We are told that "Parenteral administration is an appropriate test route for pesticides to which humans are exposed by inhalation, or for pesticides which are systemically absorbed, following ingestion" (USDHEW, 1969). It is safe to predict that, by appropriate choice of dose, concentration of solution and frequency of administration by subcutaneous route, any chemical agent can be shown to be a carcinogen or a teratogen in the rat and probably in other laboratory rodents (Goldberg, 1971).

(2) Bionetics Study: The Bionetics study began with the observation that 2,4,5-T was teratogenic and feticidal in two strains of mice when administered either subcutaneously or orally and in one strain of rats when administered orally (Courtney et al., 1970). Analyses of the sample of 2,4,5-T

that had been tested against the animals revealed the presence of 27 ±8 ppm TCDD. Subsequent study of standard 2,4,5-T containing less than 1 ppm TCDD given to rats by gavage in doses up to 24 mg/kg daily, failed to reveal evidence of teratogenic or embryotoxic effects (Emerson et al., 1970). Under similar conditions, TCDD produced no effect at a dose of 0.03 µg/kg/day while doses of 0.125 µg/kg/day or greater manifested toxicity to the fetus and at 8.0 µg/kg/day to the mother also (Sparschu et al., 1970).

(3) Evaluating Data from Animal Models: The metabolism of a test compound is a highly relevant consideration in teratogenesis. If the metabolic pathway in the test animal differs radically from that in man, then the results of a study are unlikely to be useful for the assessment of hazards arising from trace contaminants. The findings of teratogenesis or embryotoxicity has meaning only in the appropriate animal species (Goldberg, 1971). Theodor D. Sterling (1971) of the Department of Applied Mathematics and Computer Science, Washington University, St Louis, examined the difficulty of evaluating the toxicity and teratogenicity of 2,4,5-T from existing animal data. He notes that the question has been raised as to whether the herbicide 2,4,5-T is toxic and teratogenic to an extent to preclude its use, in this country at least. Sterling states, "Although we can learn a great deal from animal experiments, toxicological and teratological information from animal experiments turns out to be much less useful, especially for making broad policy decisions, than is commonly thought."

(4) Design of Recent 2,4,5-T Toxicity Studies: To quote Sterling (1971) again, "...there are less than a dozen key reports...of study on toxicity of 2,4,5-T, dating back to the early 1950's for the most part, and on its teratogenicity, mostly done in the last two years. Whereas the toxicity studies were done at some leisure and the teratogenicity studies had some aspect of emergency about them, they are indistinguishable in their lack of adequate statistical experimental design and analysis of data."

6. EVALUATION OF ENVIRONMENTAL CONTAMINATION POSSIBILITY: The possibility that an extraordinarily toxic contaminant of a widely used herbicide may be sufficiently stable in the environment and soluble in fat or other tissues to enter food chains and ultimately the human diet is worthy of consideration. It was known, of course, that 2,4,5-T does not accumulate to any significant degree in animal tissues, but data on tissue storage of dioxin were not

available. Chlorinated dibenzo-p-dioxins long have been recognized as by-products from the manufacture of certain chlorinated phenols. For example, 2,4,5-trichlorophenol is prepared industrially by the hydrolysis of 1,2,4,5-tetrachlorobenzene at elevated temperatures and pressures, a process which can also result in the formation of traces of heterocyclic impurities including 2,3,7,8-tetrachlorodibenzo-p-dioxin if temperatures are permitted to exceed 160°C and if the reaction becomes alkaline. This dioxin is toxic, teratogenic and acnegenic and its presence appears to account satisfactorily for the alleged teratogenic effects of trichlorophenol derivatives such as the herbicide 2,4,5-T.

a. Knowledge Available from Use: No proven instance of toxicity associated with 2,4,5-T intake in man has been found in agricultural or industrial workers known to have had repeated, relatively high levels of exposure to 2,4,5-T of low dioxin content. The safety factor for the general population is estimated to be several orders of magnitude greater than that for 2,4,5-T factory workers. Data are too limited for a firm conclusion, but there is no evidence to suggest that TCDD as a contaminant in 2,4,5-T is likely to be encountered by animal or man in sufficient dosage to cause toxic reactions (Advisory Committee, 1971).

b. Application of Testing: "Since most chemicals under suitable laboratory conditions could probably be demonstrated to have teratogenic effects, and certainly all could be shown to produce some toxic effects if dosage were raised high enough, it would not be reasonable to consider the demonstration of toxic effects under conditions of greatly elevated dosage sufficient grounds for prohibiting further use of a particular chemical," (Goldberg, 1971).

c. Possibility of Pyrolytically Produced Contamination: The question of the formation of TCDD as a result of the pyrolysis or burning of wood, including brush treated with 2,4,5-T, has been a matter of some concern. Langer (1973) states, "The derivatives of 2,4-D, 2,4,5-T and Silvex as well as their sodium salts and esters have not produced dioxins in pyrolytic reactions whether carried out in the solid state, in the melt, or in solution. Even after conditions of extreme hydrolysis, followed by pyrolysis we could observe only trace amounts of dioxins." Langer (1973) further stated, "Even extreme conditions such as burning of treated wood or vegetation after the use of

2,4-D, 2,4,5-T, Silvex or their derivatives is not expected to produce detectable amounts of dioxins or dibenzofuran." However, in a memorandum dated July 30, 1973, Baughman and Meselson (1973) reported that the pyrolysis of the sodium salt of 2,4,5-T at temperatures from 300 to 450°C for 30 minutes to 12 hours caused the formation TCDD ranging in concentrations from 0.1 to 0.3% (1,000 to 3,000 ppm).

d. Evaluation by EPA Advisory Committee: The data are indeed very limited. Nevertheless, certain conclusions can be made and these as made by the Advisory Committee on 2,4,5-T to the Administrator of the Environmental Protection Agency are, in part, as follows:

(1) The herbicide 2,4,5-T does not accumulate in any compartments of the biosphere, nor does it accumulate in any animal tissues or products used for human consumption.

(2) The risk of human exposure to 2,4,5-T in food, air and water is negligible.

(3) There is no indication that TCDD accumulates in air, water or plants, although it might accumulate and remain active for some time in soils after heavy application of a highly contaminated sample of 2,4,5-T.

(4) Less than 0.2% of TCDD in soil is known to be absorbed into plants.

(5) 2,4,5-T is rapidly excreted in animals studied using doses in the range of those likely to be encountered in the environment.

(6) Limited data indicate that TCDD is also eliminated, at least some by metabolic breakdown, with a half-life of 20 days.

(7) The solubility of TCDD in fat is limited which would preclude appreciable accumulation in body fat.

APPENDIX C

ANALYTICAL PROCEDURES USED BY TRW

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APPENDIX C

1. INTRODUCTION

The TRW analyses of samples acquired during the incineration of Herbicide Orange were intended to characterize the environmental acceptability of the incineration. The analytical plan discussed below is basically a Level I organic analysis. It is intended to provide quantitative information on emissions of classes of organic compounds so that important emissions do not go undetected and to provide information on the destruction efficiency of the incineration. Full documentation of Level I sampling and analysis is found in:

- "Level I Environmental Assessment," IERL Procedures Manual, Document No. EPA-60012-76-160a.
- "Combustion Source Assessment: Method and Procedures Manual for Sampling and Analysis," Draft Report to EPA-IERL-RTP, January 1977.

An overview of the methodology used for the Level I organic analyses is shown in Figure 16. This methodology deals with the preparation of the samples to provide forms suitable for analysis and with the subsequent analyses.

As indicated in this Figure, the extent of sample preparation required varies with sample type. The low molecular weight hydrocarbons, boiling at $\leq 90^{\circ}$C and reported as C1-C6 n-alkanes, are determined by gas chromatography and require no preparation. Organic liquids, such as fuel oil, also require no preparation and are placed directly into the analysis scheme. Other samples, such as the sorbent trap and burner residue, will require preparation by solvent extraction prior to analysis. Solvent extraction will separate the organic from the inorganic portions of the samples so that analysis can proceed without complications.

After extraction, the analysis of the extract or neat organic liquid proceeds in several steps. An aliquot is taken for GC analysis of hydrocarbons boiling in the range of the C7-C16 n-alkanes (90-300^{o}C). The remainder of the extract is then concentrated to 2 ml. A 0.25-ml aliquot is set aside for qualitative GC/MS analysis, and a 0.5-ml aliquot is taken and evaporated for gravimetric and IR analysis. The GC analysis provides information on the quantity of higher boiling hydrocarbons in the sample. The infrared spectrum provides information on the major types of functional groups present in the sample. The data obtained in the GC and IR analyses are complementary: most compounds detected in the GC analyses are too volatile to remain for the IR analysis, and compounds seen in the IR analysis are too involatile to be detected in the GC analysis. This complementarity also applies between the GC and LC analyses. All functional groups identified in the total sample must be accounted for in succeeding analyses. If there is sufficient material in the concentrated extracts, a portion of the extract providing not less than 50 mg is taken for liquid chromatographic separation into eight fractions. An IR spectrum is obtained on each fraction. If there is sufficient material in the LC fraction, a low resolution mass spectrum (LRMS) is measured. A low resolution mass spectrum will provide more information on compound types and, in some cases, may permit the analyst to identify specific compounds.

The remaining sections of this appendix contain procedures for sample preparation, analyses, and handling of samples for the various analyses. A separate document will address safety aspects of handling these samples.

2. EXTRACTION OF SOLID SAMPLES FOR ORGANICS

Scope and Application

The purpose of this procedure is to prepare solid samples for subsequent Level I analyses for organics. The solid samples that may be generated on this program are XAD-2 resin samples and burner head residues. Various sizes of Soxhlet extractors may be used for this procedure depending upon the size of the sample and the estimated concentration of organics in the sample. Thus, before this procedure is begun, there is a decision point to select the appropriate size of Soxhlet extractor to be used.

Summary of Method

The sample is placed or weighed into glass thimbles and extracted for 24 hours with high purity solvent. Pentane will be used to extract all samples. The resulting extracts are made to a standard volume and a small aliquot taken and set aside for GC analysis.

Sample Handling

All equipment (i.e., sample containers, spatulas, tweezers, etc.) that contacts either the solid samples or the solvent extracts is to be glass, Teflon, or stainless steel. No grease or lubricant of any kind is to be used on the ground glass joints of the extraction apparatus.

All glassware is to be rinsed with the same high purity solvent used for the sample extraction (i.e., pentane).

Apparatus

- Soxhlet extractors in a range of sizes (Ace Glass sizes A to E) with glass thimbles and condensers.
- Boiling flasks in a range of sizes from 125 ml to 500 ml with stoppers.
- Volumetric flasks in a range of sizes from 100 to 500 ml.
- Heating mantles to fit boiling flasks and variable transformers, or steam baths.
- Volumetric pipette, 2 ml, class A.
- Liquid scintillation vial with aluminum foil cap liner.
- Glass beads, 3 mm, plain.
- Filter paper, Whatman No. 1.

Reagents

- Pentane, distilled-in-glass or Nanograde.

Procedure

1. Place the sample to be extracted in the glass thimble, cover with pre-extracted glass wool. If the resin is wet with water, allow to air dry in a clean, covered glass dish.

a) XAD-2 resin; weigh directly into thimble.

b) Burner residue; weigh onto pre-extracted Whatman filter discs, fold into cone shape and place in thimble.

2. Place 5-6 glass beads in the boiling flask and fill ~1/2 full with Pentane.

3. Fit extractor onto flask and insert thimble into extractor. Label the extractor with the sample code identification. Complete assembly by attaching condenser and clamping entire apparatus in position in steam bath.

4. Supply power to the heating mantle through the variable transformer. There should be sufficient heat to result in one discharge cycle about every ten minutes. Extract each sample for 24 hours. During the first cycle, check the seating of the ground glass joints by rotating the joints while pushing the condenser/extractor and extractor/flask together. Check for solvent loss periodically throughout the extraction. Also check that the solvent is wetting the resin bed.

5. At the completion of the extraction, turn off power to the heating mantle and allow the extractor to cool. Remove the condenser. Pull out the thimble allowing all remaining solvent to drain into the extractor. Transfer the extracted sample to a glass bottle; label with the sample code identification and return to the sample bank.

6. Siphon off any solvent in the extractor into the boiling flask. Remove the extractor. Transfer the contents (minus the glass beads) of the boiling flask to an appropriate size volumetric flask. Rinse the boiling flask with three 10 ml rinses of the extraction solvent and add these rinsings to the volumetric flask. Make the volumetric flask to standard volume with the extraction solvent, label with the sample code identification, stopper and shake to blend.

7. Remove 2 ml of the extract sample with a pipette and transfer to a liquid scintillation vial. Label the flask with the sample code identification. Place both the extract sample and the 2 ml aliquot in the sample bank.

8. With every set of samples extracted, prepare a blank by following steps 2 through 7. Leave the glass thimble empty, except for the glass wool. If Whatman No. 1 filters are used in the extraction of a set of samples, then the blank is prepared by adding a pre-extracted Whatman No. 1 to the glass thimble.

3. CONCENTRATION OF ORGANIC SAMPLES

Scope and Application

The purpose of this procedure is to concentrate samples for Level 1 and Level 2 organic analyses. These samples will be in the form of solvent extracts of solid field samples and of solvent rinses of sampling hardware. During concentration volatile organic species may be lost, and thus these compounds must be determined in the aliquot samples of the neat extracts and rinses taken before concentration. The concentrations will be performed with Kuderna-Danish evaporators. Various sizes of evaporators may be used depending upon the size of the sample to be concentrated. Thus, before this procedure is begun, there is a decision point to select the appropriate size of Kuderna-Danish evaporator to be used. The extracts are dried with anhydrous sodium sulfate before concentration.

Summary of Method

The solvent extract or rinse sample is transferred to a Kuderna-Danish evaporator. The evaporator apparatus is heated on a steam bath to drive off the solvent. When the sample is sufficiently concentrated, the evaporator is removed from the steam bath and allowed to cool. The sample is then transferred to a volumetric flask.

Definitions

K-D - Kuderna-Danish evaporator
MeOH - Methanol

Sample Handling

All equipment (i.e., sample containers, flasks, etc.) that contacts either the solvent extracts and rinses or the concentrates is to be glass, Teflon, or stainless steel. No grease or lubricant of any kind is to be used on the ground glass joints of the concentration apparatus.

All glassware is to be rinsed with the same high-purity solvent with which the sample was extracted (i.e., Pentane).

Apparatus

1. Steam bath.
2. Kuderna-Danish concentrators consisting of flasks (125, 250, and 50 ml), Snyder columns, steel springs, concentrator tubes (2 ml) and adaptors as needed.
3. Glass beads, 3 mm, plain.
4. Vortex mixer.
5. Disposable Pasteur pipettes.
6. Class A pipette, 2 ml.
7. Volumetric flask, 2 ml, hexagonal base.

Reagents

- Pentane, distilled-in-glass or Nanograde.

Procedure

1. Select an appropriate size of K-D flask and attach a concentrator tube with the steel springs. Place one 3 mm glass bead in the bottom of the tube. Label the K-D flask with the sample code identification.
2. Transfer the sample to the K-D flask. Rinse the sample container with three 10 ml portions of the same high purity solvent that the sample is in. Add the rinsings to the K-D flask.
3. Attach a Snyder column to the K-D flask and clamp the flask in position over the steam bath. The solvent should boil at such a rate that the top ball of the Snyder column bounces lightly.
4. Concentrate the solvent sample to ∿5 ml.
5. Remove the K-D assembly from the bath and allow to cool. With disposable pipette, add ∿0.5 ml of the same solvent that the sample was in to the top of the Snyder column. Allow to drain into K-D flask and then remove column.
6. Rinse the sides of the K-D flask with another 0.5 ml of solvent. Remove the flask, stopper the concentrator tube and mix the tube vigorously on the Vortex mixer for 1 minute.
7. Transfer the contents of the concentrator tube to a 2 ml volumetric flask. Rinse the tube and stopper with 0.5 ml more of solvent; add these rinsings to the flask and make the flask to standard volume. Label the flask with the sample code identification.

8. With a micropipette, transfer 0.25 ml of the concentrate to a vial. This aliquot is for the qualitative GC/MS analyses. Label the vial appropriately (e.g., run No., date, next analyses).

9. Return the vial to the sample bank.

4. GRAVIMETRIC DETERMINATIONS FOR ORGANICS

Scope and Application

The purpose of this procedure is to determine the weight of nonvolatile organic species in samples for Level I organic analyses. The procedure is performed on the concentrates obtained from the Kuderna-Danish concentrations of solvent extract and rinse samples. Weights of organic residues down to 0.001 mg can be measured.

Summary of Method

An 0.5 ml aliquot of the concentrate sample is transferred with a pipette to a tared aluminum weighing dish. The sample is allowed to evaporate to dryness, stored in a desiccator overnight and weighed.

Sample Handling

All equipment that contacts either the concentrate or evaporated residue samples is to be glass, Teflon, or stainless steel. Evaporation of the samples is to be carried out in an area free from airborne dust and/or organic vapors that could contaminate the samples.

Apparatus

- Microbalance, Mettler M5 or equivalent.
- Stainless steel disiccating cabinet with gasket sealed closure.
- 500 µl syringe.
- Aluminum weighing dishes.

Reagents

- Phosphorus pentoxide, granular, reagent grade.
- Pentane, distilled-in-glass or Nanograde.

Procedure

1. Rinse the weighing dishes with the high purity Pentane. Allow them to air dry, store overnight in a stainless steel desiccator charged with P_2O_5, label with the sample code identification of the samples to be determined, weigh on the microbalance and record the tare weights.
2. Rinse a 0.5 ml pipette with methylene chloride and dry with a stream of pressurized nitrogen.
3. With the pipette, transfer 0.5 ml of the concentrate sample from its volumetric flask to the appropriately labeled weighing dish. Record the volume of the concentrate sample before removing the 0.5 ml aliquot. Repeat Step 2 before pipetting each sample.
4. Return the concentrate samples to the sample bank.
5. Allow the samples in the weighing dishes to evaporate at ambient conditions in a clean fume hood until visually dry. Store overnight in the desiccator and then weigh on the microbalance. Record this weight.
6. Place the samples in the sample bank.

Calculations

Subtract the tare weight from the final sample weight for each sample. This gives the weight of the organic residue. Multiply the residue weight by the aliquot factor to obtain the total organic residue in the concentrate sample.

$$\left(\begin{array}{c}\text{Final weight-}\\ \text{tare weight}\end{array}\right) \times \frac{\text{Total concentrate volume}}{\text{Aliquot volume}} = \begin{array}{l}\text{Total organic}\\ \text{residue (mg)}\end{array}$$

5. C7-C16 GAS CHROMATOGRAPHIC ANALYSIS

Scope and Application

Scope

This procedure defines the Level 1 analysis of environmental samples for volatile hydrocarbons. This procedure assumes an appropriate sample given to the analyst. No sample preparation is discussed.

This analysis is semiquantitative and semiqualitative. Calibrations are replicated, but analyses are not. Thus, the results are semiquantitative. The identity of peaks is not established; peaks are identified with the appropriate n-alkane.

Application

This procedure applies solely to the Level 1 C7-C16 gas chromatographic analysis of extracts or neat organic liquids. This procedure applies when the analyst has received a sample.

Range

This procedure will provide for detection of components as n-alkanes in concentrations down to 1 ng/μl with 1 μl injections.

Sensitivity

The sensitivity is defined as the shape of a plot of response (μV · sec) versus amount injected (ng/μl) and has units of μV · sec · μl/ng. The sensitivity of the procedure is 77-78 μV · sec · μl/ng for the n-alkanes **heptane to** hexadecane.

Detection Limit

The detection limit of this procedure as written is 0.7 ng/μl for a 1μl injection of n-decane. This limit is arbitrarily based on defining the minimum detectable as 100 μV · sec. This is an easier operational definition than defining the minimum detection limit to be that amount of material which yields a signal twice the noise level.

It should be noted that the instrument is capable of perhaps one hundredfold greater sensitivity. The level specified here is sufficient for Level 1 analysis.

Interferences

There are no interferences.

Limitations

Reporting Limitations — It should be noted that a typical environmental sample will contain compounds which: (a) will not elute in the specified boiling ranges and thus will not be reported and/or (b) will not elute from the column at all and will not be reported. Consequently, the other phases of Level I analysis scheme must be performed to obtain full information on the sample. Species boiling below 90°C are determined in the C1-C6 GC analysis, and species boiling above 300°C are determined in the LC analysis.

Calibration Limitations — Quantitation is based on calibration with n-decane. Data should therefore be reported as, e.g., mg C8/m^3 as n-decane. Since response varies linearly with carbon number (over a wide range the assumption may involve a 20% error), it is clear that heptane (C7) detected in a sample and quantitated as decane will be overestimated. Likewise, dodecane (C12) quantitated as decane will be underestimated. From previous data, it is estimated the error involved is of the order of 2-3%.

Detection Limitations — The sensitivity of the flame ionization detector varies from compound to compound. However, n-alkanes as a class have a greater response than other classes. Consequently, using a n-alkane as a calibrant and assuming equal responses of all other compounds tends to give low reported values.

Summary of Method

A sample (unconcentrated extract or neat organic liquid) is analyzed by gas chromatography. With boiling point-retention time and response-amount calibration curves, the data (peak retention times and peak areas) are interpreted thusly: peak areas in boiling point ranges obtained from the boiling point-retention time calibration are summed. With the response-amount calibration curve, the area sums are converted to amounts of material in the reporting ranges.

After the instrument is set up, the boiling point-retention time calibration is effected by injecting a mixture of n-C7 through n-C16 hydrocarbons and running the standard temperature program. Response-amount calibration is effected from the n-decane peak areas obtained above.

Definitions

- C7-C16 - n-alkanes: heptane through **hexadecane**
- Temperature program: room temperature to 150°C at 10°C/min.

Sample Handling and Preservation

After extraction, a 2 ml aliquot of each sample is set aside in the sample bank. For each C7-C12 GC analysis, obtain the sample far enough ahead of time for it to warm to room temperature. For example, after one analysis is started, return that sample to the sample bank and obtain the next sample.

Apparatus

A Varian 1860 gas chromatograph, equipped with dual flame ionization detectors and a linear temperature programmer is used in this procedure. Any equivalent instrument can be used provided that electrometer settings, etc., be changed appropriately. A 6-ft x 1/8-in. OD stainless steel column of 10% OV-101 on 100/120 mesh supelcoport® is used.

Procedures

Setup and Checkout —

Each day, the operator will verify the following:

1. Carrier gas first-stage regulator >100 psig.
2. Carrier gas second-stage regulator >100 psig.
3. Air first-stage regulator >100 psig.
4. Air second-stage regulator 50 ±5 psig.
5. Hydrogen first-stage regulator >100 psig.
6. Hydrogen second-stage regulator 50 ±5 psig. If any first-stage regulator indicates <100 psig, the cylinder is considered empty and will be replaced. After replacing a cylinder, all connections will be leak checked up to and including the connection to the chromatograph.
7. Verify carrier gas flow rate is 30 ±2 ml/min. Flow rate is checked at analytical column outlet after disconnection from the instrument.
8. Verify hydrogen flow rate is 30 ±2 ml/min. Flow rate is checked at gas control panel on the GC.
9. Verify air flow rate is 300 ±20 ml/min. Flow rate is checked at gas control panel on the GC.

10. Verify the electrometer is functioning properly. The electrometer will be balanced at least once each day. Bucking controls will be set as required.

11. Verify recorder and integrator are functioning properly.

12. Leak check the septa. Leak checking is effected by placing the soap bubble flow meter inlet tube over the injection port adpators. Septa are replaced after two days use.

13. Obtain list of samples to be run.

Retention Time Calibration —

To obtain the temperature ranges for reporting the results of the analyses, the chromatograph is given a normal boiling point-retention time calibration. The n-alkanes, their boiling points, and data reporting ranges are given in Table C-1.

TABLE C-1. REPORTING PROCEDURE RANGES FOR C7-C16 GC PROCEDURE

	NBP, °C	Reporting Range, °C	Report as
n-heptane	98	90-110	C7
n-octane	126	110-140	C8
n-nonane	151	140-160	C9
n-decane	174	160-180	C10
n-undecane	197	180-200	C11
n-dodecane	216	200-220	C12
n-tridecane		220-240	C13
n-tetradecane		240-260	C14
n-pentadecane		260-280	C15
n-hexadecane		280-300	C16

Preparation of Standard — A series of standard n-alkane solutions may be prepared thusly. Take 10 µl each of the pure n-C7 through n-C16 alkanes and dilute to 10 ml in a volumetric flask with pentane. Prepare three additional standards, each 10-fold more dilute than the preceding one. Use densities at 20°C.

Procedure

1. The programmer Upper Limit is set at 150°C. (If this setting does not produce a column temperature of 150°C, find the correct setting.)
2. The programmer Lower Limit is set at 20°C.
3. Verify the instrument and samples at room temperature.
4. Inject 1 µl of the n-alkane mixture.
5. Start the integrator.
6. Start the recorder.
7. Shut the oven door.
8. Change mode to Automatic; turn Lower Limit dial to 30°C to start the program.
9. Repeat Steps 1-8 a sufficient number of times so that the relative standard deviation of the retention times for each peak is <5%.

To attain the required retention time precision, both the carrier gas flow rate and temperature program specifications must be followed.

This calibration is performed at the start of an analytical program. The mixture is chromatographed at the start of each day.

Response Calibration

For the purpose of a Level 1 analysis the peak area data obtained above for n-decane is adequate.

C7-C16 GC Analysis

Apparatus

- Gas chromatograph set up and working.
- Recorder, integrator working.

- Syringe and syringe cleaning apparatus.
- Parameters: Electrometer setting is 1×10^{-10} A/mV; recorder is set at 1-in/min and 1 mV full-scale.

Procedure

1. Label chromatogram: date, sample number, etc.
2. Inject sample.
3. Start integrator, recorder, temperature.
4. Clean syringe.
5. Return sample: obtain new sample.
6. When analysis is finished allow instrument to cool. Turn chromatograph and integrator output and data sheet over to data analyst.

Syringe Cleaning

Apparatus

- Hamilton syringe cleaner connected to water aspirator.
- Reagent grade pentane and methylene chloride.
- Disposable pipettes and medicine dropper bulbs.

Procedure

1. Remove plunger from syringe.
2. Insert syringe into cleaner; turn on aspirator.
3. Fill pipette with pentane; run pentane through syringe.
4. Repeat with methylene chloride from a separate pipette.
5. Fill pipette with pentane; flush plunger with pentane.
6. Repeat with methylene chloride.

Calculations

Boiling Point — Retention Time Calibration

The required data for this calibration are on the data sheet. The data reduction is performed thusly:

1. Average the retention times and calculate relative standard deviations for each n-hydrocarbon.

2. Plot average retention times as abscissae versus normal boiling points as ordinates.

3. Draw in calibration curve.

4. Locate and record retention times corresponding to boiling ranges (90-110°, 110-140°, 140-160°, 160-180°, 180-200°, 200-220°, 220-240°, 240-260°, 260-280°, 280-300°C).

Response-Amount Calibration

The required data for this calibration are on the data sheet. The data reduction is performed thusly:

1. Average the area response of decane from each standard and calculate relative standard deviations.

2. Plot response ($\mu V \cdot sec$) as ordinate versus ng/μl as abscissae.

3. Draw in the curve. Perform least squares regression and obtain slope ($\mu V \cdot sec \cdot \mu l/ng$).

C7-C16 Analysis

The required data from the analyses are on the data sheet. The data reduction is performed thusly:

1. Sum the areas of peaks in the proper retention time ranges.

2. Convert areas ($\mu V \cdot sec$) to ng/μl by dividing by the proper weight response ($\mu V \cdot sec \cdot \mu l/ng$).

3. Obtain total volume of extract. Multiply each weight by total extract volume to get weight of species in each range in the sample.

4. If the volume of gas sampled or the total weight of sample acquired is available, convert result of Step 3 above to mg/m^3.

Precision and Accuracy

Even a crude error propagation analysis is beyond the scope of this procedure. With reasonable care, peak area reproducibility of a standard should be of the order of 1% RSD. The relative standard deviation of the sum of all peaks in a fairly complex waste might be of the order of 5-10%. Accuracy is more difficult to assess. With good analytical technique, accuracy and precision should be of the order of 10-20%.

6. LIQUID CHROMATOGRAPHIC SEPARATIONS

Scope and Application

Scope

This procedure is designed to give a separation of a sample into eight reasonably distinct classes of compounds.

Application

This procedure applies to Level 1 analyses and to those samples which contain a minimum of 50 mg of nonvolatile organics.

Range

Samples may range from 50 to 100 mg. The optimum size is considered to be 100 mg.

Sensitivity

As defined, this procedure will permit the analyst to measure as low as 1 µg of residue.

Detection Limit

The detection limit is 1 µg of residue.

Interferences

There are no interferences.

Limitations

Compounds of too high polarity or molecular weight will not be eluted from the column since this procedure is a compromise between cost and data acquisition. Also, compounds of too low molecular weight will be evaporated along with the sample solvent during sample preparation.

Summary of Method

A sample of weighing from 50-100 mg is placed on a silica gel liquid chromatographic column. A series of eight (8) eluents are employed to separate the sample into eight nominally distinct classes of compounds for further analyses.

Sample Handling and Preservation

The traveler for this analysis will specify the volume of concentrated extract to be taken to give an appropriate weight of material for the separation. This specified volume is withdrawn with a graduated pipette. Then the sample is returned to storage.

Apparatus

- Column: 200 mm x 10.5 mm ID, glass with Teflon stopcock.
- Adsorbent: Davison Silica Gel, 60-200 mesh, Grade 950
- Graduated cylinders: 25 ml and 10 ml.
- Aluminum weighing dishes: precleaned.
- Volumetric Flasks: 2-25 ml and 6-10 ml, precleaned.
- Beakers: size depends on sample size.
- Microspatula.
- Disposable pipettes, medicine droppers.
- Glass wool.
- Funnel.

Reagents

- Solvents are all "reagent" grade or better.

Eluents

1-pentane	Collect 25 ml
2-20% CH_2Cl_2/Pentane	Collect 10 ml
3-50% CH_2Cl_2/Pentane	Collect 10 ml
4-CH_2Cl_2	Collect 10 ml
5-5% CH_3OH/CH_2Cl_2	Collect 10 ml
6-20% CH_3OH/CH_2Cl_2	Collect 10 ml
7-50% CH_2OH/CH_2Cl_2	Collect 10 ml
8-conc. $HCl/CH_3OH/CH_2Cl_2$ (5+70+30)	Collect 25 ml

Procedure

The volume of samples expected during the Source Assessment program means that a reasonable number of LC separations will be performed. Six columns is the maximum that will be operated by any single analyst. Of these six columns, one will be a blank (no sample added to column).

The data to be obtained are:

- Weight of sample added to column.
- Weights of fractions after they have been evaporated in aluminum dishes to constant weight.

Data are indicated on the data sheet.

Sample Preparation —

1. Obtain volume of sample extract calculated to give either the optimum weight, 100 mg or a weight not less than 50 mg.
2. Obtain a precleaned and labeled beaker of at least 30% greater capacity than the required volume of sample. Pipette the sample into the beaker, cover loosely with a watch glass, set in hood and allow solvent to come to near dryness.
3. Quantitatively transfer the near-dry sample into a clean, tared, and labeled glass weighing boat. Rinse the beaker with methylene chloride into boat.
4. Check the weight of the boat twice daily until the weight is stable. This is the sample weight.
5. Add 0.5-1.0 g of freshly activated silica gel to the weighing boat and mix thoroughly with a sample using a microspatula.

Activation of Silica Gel

Activate the silica gel for 2 hours in a drying oven at 110°C. Cool and store in a desiccator.

Column Packing

1. Plug the outlet of the precleaned column with glass wool. Pack the column with 6.5 grams of freshly activated silica gel. For freshly activated silica gel, this weight occupies 9 ml in a 10 ml graduated cylinder. Tap the column briefly with the microspatula to compact the bed.
2. Take a 50 ml volume of pentane and pour it through the column until the bed is homogeneous, free of any cracks, and free of any air bubbles. Continue pentane flow until the 50 ml volume is used. The pentane level should be at the top of the bed, hereafter called the origin. NEVER ALLOW THE TOP OF THE BED TO GO DRY.

Elution of Sample

1. Position a 25-ml graduated cylinder as a receiver under the column. Transfer the prepared sample into the column. Rinse weighing funnel into the column three times with 1 ml of pentane each time. Begin adding 22 ml of pentane, and start elution at a flow rate not greater than 1 ml/min. Collect 22 ml of pentane, adding more to the column if necessary. Do not allow pentane to go below the top of the bed.

2. When 22 ml of pentane are collected, the pentane level is at the top of the bed. In a graduated cylinder, take 10 ml of Eluent No. 2. Rinse the glass weighing boat with 2 ml of Eluent No. 2 into the column. Add the remaining 8 ml of Eluent No. 2 into the column and start eluting. Collect 3 ml of eluent in the 25 ml receiver. Stop elution. This is the first fraction. Label this and succeeding fractions as they are collected.

3. After the first fraction has been collected, place a 10 ml volumetric flask under the column as receiver. Start elution and collect 10 ml of Fraction 2, adding small amount of Eluent No. 2, 20% CH_2Cl_2 in pentane, as necessary. At the end of collection, the solvent level must be at the origin. This is fraction No. 2.

4. Replace the receiver with another 10-ml volumetric flask. Take 10 ml of Eluent No. 3, 50% CH_2Cl_2/pentane in a graduated cylinder. Rinse glass weighing boat with 2 ml into the column. Start elution, adding remaining solvent. Collect 10 ml of Fraction No. 3, adding small amounts of the solvent if necessary. Again, the solvent level must be at the origin.

5. Repeat step 4 with the remaining eluents:
   - CH_2Cl_2, 10 ml
   - 5% CH_3OH/CH_2Cl_2, 10 ml
   - 20% CH_3OH/CH_2Cl_2, 10 ml
   - 50% CH_3OH/CH_2Cl_2, 10 ml
   - Conc. $HCl/CH_3/OH/CH_2Cl_2$ (5:70:30), 25 ml

6. In the area specified for solvent evaporation, quantitatively transfer sample Fractions 1-7 into precleaned, tared, and labeled aluminum microweighing dishes. Fraction 8 is transferred into a small tared and labeled glass petri dish. Quantitative transfer is finally effected by rinsing each sample fraction receiver two times with 2-ml volumes of methylene chloride.

7. The solvents are allowed to evaporate. When Fraction 8 appears dry, dissolve it in CH_2Cl_2 and transfer to a second tared and labeled glass petri dish. This transfer is intended to separate organics from silica from the column. When all fractions appear dry, weigh twice daily until stability occurs: ±0.002 mg.

8. After final weights are obtained, store the dishes in a desiccator and return to sample controller.

Calculations

Data collected are:

- Weights of sample until constant weight was achieved.
- Weights of the fraction until constant weights were achieved.
- Weights of the blank fractions until constant weights were achieved.

The weights of the sample fraction are corrected for the weights of the corresponding blank fractions.

Data transmitted to program management will be the corrected fraction weights. For internal use, the percentage overall recovery and weight percentage distribution in the fractions will also be calculated.

Accuracy and Precision

Presently there are no data by which this procedure can be evaluated. Accuracy and precision appear to be sufficient for Level 1 analyses.

7. INFRARED ANALYSIS

Scope and Application

This procedure is used to determine the functional group types present in an organic sample of LC fraction of a partitioned sample. The IR data, when interpreted, provide information on functionality, e.g., carbonyl, aromatic hydrocarbon, alcohol, amine, aliphatic hydrocarbon, halogenated organic, etc. Compound information is possible only when that compound is known to be present as a dominant constituent in the sample. However, such foreknowledge is normally unlikely.

Sample amounts required for this analysis are in the milligram (mg) range. A compound must be present in the sample at about 5%-10% (w/w) or more in order for the stronger functional groups of the compound to become apparent for interpretive purposes. Organic solvents, water and some inorganic materials cause interferences. Water and other substances may also cause a decrease in the quality (e.g., resolution of a spectrum, sensitivity) of the analysis.

Summary of Method

The sample or LC fraction, after evaporation, is either (1) taken up in a small amount of methylene chloride and transferred to a KBr salt plate, or (2) mixed in a KBr mull and pressed into a pellet. A grating IR spectrophotometer is used to scan the sample in the IR region from 2.5 to 25 microns. The spectrum is then interpreted to determine functional groups types in the sample.

Definitions

Sample cell — Two KBr salt plates with the sample sandwiched in between.

Sample Handling and Preservation

These samples are typically found in the aluminum weighing dishes in which solvent, water or other volatile matter has been removed by evaporation or desiccation. The samples should be covered and stored in a refrigerator when not being used. All glassware, implements, etc., should be carefully cleaned, solvent rinsed, and dried before use in this procedure. Contact of sample with hands, fingers and other sources of outside contamination shall be avoided.

Equipment

- Infrared (IR) spectrophotometer, grating dispersion. Perkin-Elmer 521 or equivalent.
- KBr salt plates — Configured to fit sample holder of spectrophotometer. Transparent to the IR in the 2.5 to 15 micron region.
- KBr pellet press — Hydraulic type is preferred (Carver Model C or equivalent) but hand-held devices are acceptable, e.g., Perkin-Elmer 186-0436 or equivalent.
- KBr pellet die — To prepare 13 mm diameter or equivalent pellet to contain approximately 1 mg of sample. Perkin-Elmer 186-00250 or equivalent.
- Pipette, Pasteur, disposable — Sargent S-69647-30 or equivalent.
- Standard polystyrene film sample — Normally supplied by instrument manufacturer.

Reagents

- Methylene Chloride — Spectrophotometric grade
- KBr powder — spectrograde

Procedure

It is possible that two sample forms will occur: (1) an amorphous mass (expected to be the typical sample) and (2) a crystalline or powdery mass. Separate procedures are desirable for these two forms in order to obtain the best available spectra.

Procedure for Amorphous Material

Add a few drops of methylene chloride to solubilize the sample slightly and mix with the tip of a disposable Pasteur pipette. Then using the pipette, take a few drops of this material and transfer to a clean KBr salt plate. Allow the solvent to evaporate at ambient temperature, and then press the other salt plate to spread the sample throughout the area where the IR beam impinges on the plate. Mount the sample cell in the sample compartment of the spectrophotometer previously prepared according to the manufacturer's manual and check for resolution (see Note on Resolution). Scan the region from 2.5 to 15 microns using the parameters in Table C-2. The sample size should be adjusted so that the most intense peak in the spectrum has a percent transmission of between 5 to 15 percent. If the spectrum is too weak, more sample must be added, the solvent evaporated, the plates re-assembled, and the spectrum rerun as above. If the spectrum is too strong, i.e., peaks with less than 5 percent, excess sample must be removed by wiping the plates and rerun as above.

TABLE C-2. INSTRUMENT SCANNING PARAMETERS

Scan time for 2.5 - 15 microns	8-10 minutes
Scale expansion	1X
Transmittance/absorbance mode switch	Transmittance

Procedure for Crystalline Material –

The preferable IR sample preparation for crystalline or powdery materials is a KBr pellet. Mix the sample thoroughly to ensure homogeneity. Take about 1 mg of sample and mix with typically 300 mg of KBr powder (amounts can be adjusted to meet specifications of the KBr pellet die used). A small mortar and pestle can be used to mix the sample, but the use of a sample amalgamator or motorized grinder is probably preferable. Add the mixture to the pellet die, assemble and press the pellet according to the manufacturer's instructions, and check for resolution (see Note below). The resulting pellet is placed in the instrument's sample stage, and it is scanned using the parameters in Table C-1. Normally, the ratio of 1 mg to 300 mg KBr powder yields a spectrum of the proper intensity. However, more sample can be added, or the pellet diluted with more KBr, reground, and rerun as required.

Note on Resolution

The instrument settings affecting resolution will vary somewhat with different instrument manufacturers and models. The instrument preparation shall include a test scan using a standard polystyrene film. Comparison of the obtained spectra with an acceptably resolved standard spectra for the standard will demonstrate that the instrument is performing acceptably. This resolution check shall be performed at least once each day that samples are analyzed.

The resulting spectra are interpreted by one with training and experience in this field. Access to the several general and special literature sources on IR interpretation are assumed.

Calculations

Calculations are not required in this qualitative technique.

Accuracy and Precision

Values cannot be given owing to (1) the variable nature of the sample and (2) the qualitative, not quantitative, nature of the analyses.

8. LOW RESOLUTION MASS SPECTROMETRIC ANALYSIS

Scope and Application

This procedure is a survey analysis used to determine compound types in an organic sample or in an LC fraction of a sample. The analyst is specifically searching for hazardous compounds or compounds which may be generally considered toxic. Examples are aromatic hydrocarbons and chlorinated organics. Analysis using different sample ionizing parameters results in molecular weight data which, combined with IR and sample data, can provide specific compound category identifications on a "most probable" basis.

The MS instrument when used in this procedure has a sensitivity such that 1 nanogram or less presented to the ionizing chamber can result in a full spectrum with a signal to noise ratio of 10:1. A dynamic range of 250,000 or better is achievable.

However, the detection limit for a specific compound related to the size of an air sample or liquid sample will vary widely depending on the types and amounts of species in the mixture. This is because of the interfering effect that each compound has on the spectral data. The impact of this interference phenomenon can be reduced by lowering the ionization voltage resulting in spectra containing largely molecular ions. This is discussed later.

Summary of Method

The samples are dissolved in a small amount of solvent and placed in a sample cup or capillary of the direct insertion probe using a syringe. More volatile samples are weighed into a cuvette for assembly into a batch or liquid inlet system. The probe or cuvette is temperature programmed from ambient temperature up to 300°C. Periodic MS scans are taken of the volatilized sample during the program using either an ionizing voltage of 70eV or a lower range (10-15eV) or both. This is at the discretion of the operator depending upon the real time data he is observing. The resulting spectra are interpreted using reference compound spectra libraries, IR data, and other chemical information known about the sample. The result is compound type information, groups of homologous compounds, and in some cases specific compounds.

Definitions

- LRMS — Low resolution mass spectrometry. Low resolution in this sense means that typically only unit mass data are used, and the instrument resolution can separate adjacent peaks differing by one atomic mass unit (AMU).
- LC — Liquid Chromatography

- MS — Mass Spectrometer
- Molecular ion — The ionized molecule, unfragmented, which when detected, provides the molecular weight of the molecule.
- "Most probable" — This term refers to the confidence in a compound identification based upon all chemical and spectroscopic information known about the sample.

Sample Handling and Preservation

These samples are usually found as residues in aluminum dishes, from which extraction and separation solvents have been removed, along with water, by evaporation and desiccation. On some occasions, the residue is somewhat fluid due to a rather nonvolatile liquid being present. These samples should be stored in a refrigerator when not being used. All dishes and implements must be carefully washed in warm soapy water, rinsed several times with water, rinsed in pure organic solvents such as hexane, acetone, or methylene chloride and dried. Contact of the sample with hands, fingers and other sources of outside contamination must be avoided.

Apparatus

Finnigan — Model 4023 Automated GC/MS

Several other quadrupole or magnetic sector MS instruments, automated or manual, are available to perform this analysis. Minimum requirements are:

- Resolution of at least 1000 over the 40 to 1000 AMU range.
- A solid inlet system.
- A batch inlet system for liquid samples. (This can be the gas chromatograph.)
- Variable ionization voltages from zero to at least 70 eV.
- Electron multiplier detection system.

Reagents

Supplies of the following solvents, Pesticide Grade, Distilled-in-Glass®, or equivalent should be kept in 1- or 2-liter quantities. These solvents will be used to solubilize the residues as required for homogenization of the sample and its placement in the solid probe capillary. The choice of the proper solvent(s) rests with the operator and his knowledge of the sample (e.g., which LC fraction, IR data, solubilities, etc.):

- Pentane
- Methylene chloride
- Methanol
- Petroleum ether
- Diethyl ether

Procedure

Instrument Preparation

The procedure assumes that the MS has been activated per the manufacturer's manual and is prepared to gather and record data. Briefly summarized this procedure includes:

- Monitoring all applicable pressures and confirming that proper vacuum levels are being achieved.
- Checking all applicable temperatures and making adjustments as necessary.
- Checking performance of ionizer.
- Optimizing resolution/sensitivity.
- Confirming that all electronics associated with data gathering are functioning properly.

When all the necessary checks have been performed, then proceed with the analysis of a sample.

Analysis of the Sample

1. Place 1 microgram or less of the sample under test in a solid probe glass capillary. The sample may be inserted as a solid but it is preferable to first dissolve it in a solvent. Both techniques, described in steps (a) and (b) below, ensure controlled evaporation of the sample into the ion source. Avoid touching or otherwise contaminating the solid probe tip or the glass capillary. Always wear clean nylon gloves or equivalent when handling the solid probe tip, and use forceps to handle the glass capillaries.

   a. If the sample is in solution, the solvent must be evaporated prior to inserting the sample into the mass spectrometer. Do this by gently heating the glass capillary.

Placing the capillary under a heat lamp or appliance such as a hair dryer is acceptable.

b. If the sample is inserted as a solid, it may occasionally blow out of the capillary when heated too quickly. To prevent this, place the solid at the bottom of the glass capillary and then insert a small quantity of silanized glass wool (pyrex) over the sample.

CAUTION: Sample size should be 1 µg or less to minimize contamination of the ion source.

2. Place the capillary tube into the end of the solid probe by pushing the retaining spring aside then releasing it to hold the capillary tube in place.

3. Insert the solid probe tip into the slip vacuum seal at the entrance of the solid inlet, and push the solid probe in until the index pin in the guide rod snaps into the hold in the tube.

4. Tighten the slip vacuum seal by turning the black knob clockwise.

5. Evacuate the inlet solid and monitor the inlet pressure, and when it is reduced to 0.04 torr stop the evacuation.

6. Open the solid probe valve by rotating the crank counterclockwise.

7. Depress the locking button on the guide rod, and slowly push in the solid probe to the full length of travel.

8. Connect one end of the solid probe heating cable to the socket in the handle of the probe. Connect the other end of the cable to the connector labeled Program.

9. Prepare the mass spectrometer for acquiring data. The parameters which must be entered into the MS controller include the following:

   Solid probe temperature — Program rate

   Mass range — 40-600

   Scan time for mass range —

   Time interval between scanning —

   Record this data in the instrument log book.

10. Set the temperature control for the temperature range from ambient to 300°C and the desired temperature program rate. The rate may be adjusted by the operator at his discretion to control sample sputtering, etc. Depress the Solid Probe Selector push-button under the temperature readout to monitor the probe temperature.

11. Start the scanning sequence and data acquisition of the mass spec/computer to acquire data in accordance with the parameters set in Step 9. Then depress the Solid Probe push-button to start the heating cycle. The probe will now heat at the selected rate while MS data is acquired, processed, and stored in the computer.

12. When the probe temperature reaches 300°C, stop data acquisition by pressing the appropriate computer stops. Turn the solid probe heater off and allow the probe to cool. Then disconnect the cable from the probe handle and pull the probe out to the stop. Close the solid inlet valve by turning the handle clockwise. Loosen the slip vacuum seal knob. Push down on the stop pin in the guide rod and withdraw the probe.

Elements of data interpretation are presented here as a checklist of things to consider.

1. Study all available information about the sample.

2. Verify that the mass counter is accurate.

3. Study the general appearance of the spectrum, e.g., molecular stability, isotopic abundances indicating some heteroatoms, rings plus double bonds, characteristic ions.

4. Identify neutral fragments accompanying high mass in formation (including metastable peaks, if available).

5. Postulate classes of compounds and test against reference spectra for the same or similar compounds, or spectra predicted from mechanisms of ion decompositions. Examine the data from analyses run with the low ionization potentials.

In the analysis mode where low ionization voltages are used (10-15 eV), the intensity of the peaks caused by apparent molecular ions of "most probable" identified compounds can be examined to provide an estimate of the abundances of identified species. Only an estimate can be given because the production and stability of molecular ions are not equal for all compounds. This type of estimation is significantly more error prone when 70 eV ionization energies are used. The estimation procedure is carried out by normalizing all of the molecular ion peaks and reporting each species as a fraction of the total. Reported levels are limited to major, minor, and trace designations.

Calculation of Approximate Intensities

Estimates of compound classes, group types or "most probable" identified compounds are made using the following calculation based on normalization:

$$\%X = \frac{h_x f_x}{\Sigma^n h_n f_n} (100)$$

where:

$\%X$ = Mole percent composition of a compound or group of compounds making up a class

h_x = Sum of intensities and/or peak height(s) caused by compound(s)

h_n = All observed peak heights and/or intensities

f_x and f_n = Instrument response factors which shall be considered to be equal to 1.

Accuracy and Precision

This qualitative method is only roughly quantitative. The precision associated with an LRMS analysis of a solid sample has not been established. The true value of a quantitative estimate should be expected to vary by a factor of plus or minus 3. That is, the true value of X lies somewhere between one-third and three times the reported value.

9. QUALITATIVE ANALYSIS BY GC/MS

Scope and Application

Scope

This method is for the qualitative analysis of samples derived from the incineration of Herbicide Orange. The quantitation of 2,4-D and 2,4,5-T butyl esters is provided; the quantitation of any other species found in the analysis of these samples will be estimates. The manner in which the GC/MS data is gathered and stored will enable the analyst to search for compounds known to be present in Herbicide Orange (and which elute from the GC) and to identify any other compound found. **Table 11** shows the average composition of four lots of Herbicide Orange.(3)

Sensitivity

The GC/MS sensitivity varies with several parameters including the type of compound, instrument internal cleanliness, resolution of closely eluting peaks, etc. Under "everyday" operating conditions 10 nanograms (ng) eluting in a peak about 5 seconds wide will yield an MS signal with a usable signal-to-noise ratio of greater than 10 to 1. A dynamic range of greater than 100,000 is achievable.

Detection Limit

There will typically have to be at least 100 μg of material extracted from a sample and concentrated to 10 ml of solution. This presumes a 1μl sample injection volume and the typical instrument sensitivity specified above.

Interferences

This analysis is performed using the MS in a Total Ion Monitoring mode (TIM). In this mode, all ion fragments in a specified mass range are monitored and, as a result, all compounds are detected if they elute from the GC in detectable quantities. Because 2,4-D and 2,4,5-T are expected to be present in higher quantities than other species, some spectral interference may result if other species elute at or near the same time as 2,4-D and 2,4,5-T. Computer data manipulation techniques, such as ion mapping, can minimize interferences. Information exists on the chemical composition of Herbicide Orange, and the known herbicide components will be specifically sought.

Summary of Method

This is a combined gas chromotography/mass spectrometry method (GC/MS). Microliter quantities of concentrated sample extracts are used for this analysis. The concentrated extracts result from the extraction of the various samples obtained from the sampling activity. The extraction and concentration procedures are specified elsewhere in this document.

Microliter sized samples are injected onto a gas chromatographic column and are separated by the differences in the retention characteristics between the sample components and the column material. As the mixture components elute from the column, they are transported via an instrument interface to the mass spectrometer. The MS ionizes the components and analyzes the fragments in a 60-650 AMU range. The signal from the mass spectrometer is stored in the memory of a computer. The computer than searches the stored spectra for close matches to a library set of spectra. Peaks other than 2,4-D and 2,4,5-T are not specifically quantitated, but relative abudance estimates are reported.

Definitions

ES - External Standard
TIM - Total Ion Monitoring

Sample Handling and Preservation

These samples are organic solutions resulting from extraction and concentration. They are contained in stoppered or septum sealed vials and are 0.25 ml in volume. These samples are presumed to contain toxic materials, so due care shall be used in handling all samples and standards. Gloves and fume hoods are appropriate considerations.

Apparatus

This section specifies the major pieces of required apparatus. A normal complement of glassware and implements is assumed.

Automated GC/MS — Finnigan Corporation, Model 4023 — Several other quadruple or magnetic sector instruments, computer driven, are available to perform this analysis. Basic required capabilities include:

- Resolution sufficient to obtain unit mass peaks in the 50-650 range (typically 1000)
- Capability for 6-mm ID glass packed columns and a sample enrichment device to achieve yields and efficiencies such that the 10 ng total instrument sensitivity is achieved.
- Electron multiplier detection system.
- Total Ion Monitoring capability in the 50-650 range.

Interactive Data System — Capable of gathering and storing TIM data, enhancing data, generating total ion chromatograms, and spectral searching for library spectra of known compounds.

GC column — 6-foot, glass column containing 3% OV-101 on 100-120 mesh Chromosorb WHP, or equivalent.

GC injection syringes — 10 μl with 0.2 μl graduations.

Analytical balance — capable of weighing ±0.05 mg.

Reagents

Supplies of the following solvents, pesticide grade, Distilled-in-Glass®, Nanograde® or equivalent should be kept at hand in 1- or 2-liter quantities. These solvents will be used to prepare analytical standards, make dilutions, do solvent replacement or other similar activities as required.

- Benzene
- Pentane
- Methylene chloride
- Methanol
- Acetone
- Petroleum ether
- Hexane
- Diethyl ether
- 2,4-D butyl ester, EPA Reference Standard No. 2980
- 2,4,5-T butyl ester, EPA Reference Standard No. 6870.

Procedure

The samples will have been concentrated as greatly as practicable. The samples, 0.25 ml, will have been placed in vials at the end of the concentration procedure (Section 5.4) and are then available for analysis.

Preparation of Standard Solutions

It is intended to quantitate only 2,4-D and 2,4,5-T mixed esters in these samples. At the required destruction efficiency, the sorbent traps are expected to yield extracts having 2,4-D and 2,4,5-T concentrations of about 200 μg/μl each. These samples may be diluted. Reference materials (2,4-D and 2,4,5-T butyl esters) are obtained from the U.S. EPA. Standards will be prepared in benzene at levels of 200, 20, 2, and 0.2 μg/μl. The GC/MS will be calibrated with these standards, and a curve of peak area versus weight of standard will be prepared.

Preparation of the GC/MS Instrument

The gas chromatograph shall be prepared according to the manufacturer's operating manual. Key operating parameters to be used are as follows:

Column - 3% OV-101 on 100-120 mesh Chromosorb WHP, 6-ft x 2-mm ID, glass 100-120

Carrier Gas - Helium, zero grade at 20 ml/min

Oven Temperature - 50-280°C programmed at 4°C/min

Injector Temperature - TBD

Transfer Lines and Separator - 200° - 220°C

The mass spectrometer (MS) will be prepared according to the manufacturer's operating manual. Briefly summarized, this procedure includes:

- Monitoring all applicable pressures and confirming that proper vacuum levels are being achieved. Proper levels are specified in the manual.
- Checking all applicable temperatures and making adjustments as necessary:

  Ionizer - TBD
  Main chamber - TBD
  Electron multiplier - TBD

- Checking performance of ionizer.
- Optimizing resolution/sensitivity.
- Confirming that all electronics associated with data gathering are functioning properly.

Important MS parameters to be set are as follows:

Electron energy	70 eV
Ionizing energy	1 milliamp, may be changed to 0.2 mA
Electron multiplier	2.5 kV, or as required to optimize signal-to-noise ratio
Sensitivity	10^{-5} amps/volt
Source pressure	5×10^{-6} torr or less

Data and record parameters in instrument log book.

Preparation of Computer/Data Acquisition System — Use the Operating Manual for the computer to select the operating parameters for data collection, storage and processing time.

Mass range	40 - 400 AMU
Spectral scan time	∿5 sec.
Ion abundance threshold	TBD

Starting the Analysis

When all preparations have been completed, inject the sample into the gas chromatograph which is in the solvent divert mode. At a given time after injection, the solvent divert valve directs the sample components eluting from the GC into the MS. Concurrently, a signal is set to start the MS scanning sequence and data acquisition of the mass spec/computer to acquire and store data in accordance with the pre-programmed parameters. The instrument will then gather and store data over the time interval during which the individual in the sample will elute. The analysis will continue for a pre-set duration or until the operator intervenes. The system will be programmed to stop the analysis after ∿50 minutes have elapsed from time of injection. The elution time and temperature program may be changed as required by the species present in the sample.

Data Processing

The data system is directed to construct a total ion chromatogram from the acquired data. Moreover, the system is ordered to enhance the data and/or to perform background subtractions as required and then to search the mass spectral library for matches to peaks in the reconstructed chromatogram. All matches are evaluated visually by the operator. Butyl esters of 2,4-D and 2,4,5-T will be quantitated by comparison with the standards. Other species will be quantitated by inference.

APPENDIX D

THERMOCHEMICAL ANALYSIS AND ESTIMATION OF EMISSION LEVELS

APPENDIX D — INDEX

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APPENDIX D

1. EQUILIBRIUM PRODUCT DISTRIBUTION ANALYSES

The purpose of the equilibrium product theoretical computation is to define the practical bounds for the safe operation of the Vulcanus incinerators during the destruction of Herbicide Orange. In the combustion studies, Herbicide Orange was assumed to have the following composition: c, 49.1 wt %; H, 4.6 wt %; O, 16.4 wt %; Cl 29.9 wt %. The equilibrium product distributions from Herbicide Orange incineration were examined at four temperature levels (1000°C, 1250°C, 1500°C, and adiabatic flame temperature) and for four air/waste ratios. As indicated in Table D-1, the four air/waste ratios examined correspond to approximately 3.0, 6.5, and 10.0 mole percent of oxygen in the stack gas and to a case where only 80 percent of the air required for stoichiometric combustion is fed. The 80 percent stoichiometric air case was designed to determine the equilibrium product distribution under oxygen deficient conditions.

TABLE D-1. AIR/HERBICIDE ORANGE RATIOS EXAMINED IN EQUILIBRIUM PRODUCT DISTRIBUTION ANALYSIS

Mole % O_2 in Stack	% Excess Air*	$\frac{M^3 \text{ Air}^\dagger}{\text{Kg Orange}}$
~3.0%	18.44%	6.235
~6.5%	49.61%	7.876
~10.0%	100.60%	10.560
0%	-20%	4.211

*% Excess air = $\left(\frac{\text{Actual amount of air fed-stoichiometric air req'd}}{\text{Stoichiometric amount of air req'd}}\right)$ x 100%

†M^3 air at 25°C (77°F)

The equilibrium product distribution from the combustion of Herbicide Orange was determined using the TRW Chemical Analysis Program (CAP). This program is capable of simultaneously considering a maximum of 200 gaseous products together with a maximum of 20 condensed species, and is based on solving a system of simultaneous equations of elemental mass balances and a pressure match which satisfies equilibrium relationships for all reactions and minimizes the system free energy. The results of the thermochemical computations are summarized in Table D-2. The effects of air/waste ratio and temperature on the equilibrium product distribution are discussed below.

Effects of Air/Waste Ratio

As indicated in Table D-2, the major equilibrium products under excess air conditions are CO_2, H_2O, HCl, N_2 and O_2. The major equilibrium products under oxygen deficient conditions are CO, CO_2, H_2, H_2O, HCl, N_2 and O_2. In addition, the formation of CO_2, Cl, Cl_2, H_2O, O_2 and OH is favored at higher air/waste ratios, and the formation of CO and H_2 is favored at lower air/waste ratios. In particular, CO will appear in considerable concentrations when the air supply is below the stoichiometric requirement. At an air/Herbicide Orange feed ratio of 4.211, for example, the equilibrium CO concentrations are in the 6.6 to 7.9 mole percent range. Even under excess air conditions, however, improper mixing of combustibles such as CO and air will lead to localized air deficient pockets and result in high CO emission levels. Thus measured CO concentrations at the incinerator exit can be used to provide a good indication of the degree of mixing between combustibles and air in the incinerator. Since the percent combustion efficient = (1 - CO concentration/CO_2 concentration) x 100, the requirement for high combustion efficiency also implies low CO concentration and a high degree of mixing between combustibles and air. In this sense, combustion efficiency as defined here can also be interpreted as a measure of the degree of mixing between combustibles and air.

Effects of Temperature

The results of the thermochemical calculations indicate that the formation of CO, Cl, NO and OH is favored by increasing the reaction temperature, whereas the formation of CO_2 and Cl_2 is favored by decreasing the reaction temperature. Increasing the reaction temperature also favors the formation of H_2 under excess air conditions and the formation of H_2O under oxygen deficient conditions. In

TABLE D-2. EQUILIBRIUM PRODUCT FROM THE COMBUSTION OF HERBICIDE ORANGE

Air/Orange Ratio $(\frac{M^3\ Air}{kg\ waste})$	Temperature	Species Concentration in Gas Phase, Mole Fraction										
		CO	CO_2	H_2	H_2O	HCl	N_2	Cl	Cl_2	NO	O_2	OH
6.235	1000°C	7.437-8	1.472-1	2.089-8	6.803-2	2.984-2	7.247-1	1.244-4	1.658-4	1.314-4	2.982-2	3.722-6
	1250°C	5.820-6	1.471-1	1.009-6	6.811-2	2.962-2	7.244-1	5.424-4	6.432-5	5.322-4	2.955-2	4.670-5
	1500°C	1.323-4	1.469-1	1.671-5	6.840-2	2.869-2	7.237-1	1.520-3	3.043-5	1.440-3	2.886-2	2.865-4
	1841°C†	2.776-3	1.439-1	2.678-4	6.845-2	2.619-2	7.206-1	3.971-3	1.286-5	3.814-3	2.797-2	1.701-3
7.876	1000°C	4.065-8	1.185-1	1.144-8	5.488-2	2.388-2	7.374-1	1.346-4	1.940-4	1.954-4	6.477-2	4.058-6
	1250°C	3.176-6	1.185-1	5.517-7	5.495-2	2.366-2	7.370-1	5.861-4	7.509-5	7.924-4	6.439-2	5.096-5
	1500°C	7.191-5	1.184-1	9.113-6	5.527-2	2.268-2	7.360-1	1.627-3	3489-5	2.152-3	6.341-2	3.135-4
	1568°C†	1.454-4	1.183-1	1.723-5	5.537-2	2.228-2	7.356-1	2.033-3	2.870-5	2.694 3	6.301-2	4.725-4
10.560	1000°C	2.485-8	8.993-2	6.998-9	4.168-2	1.802-2	7.500-1	1.298-4	1.805-4	2.446-4	9.975-2	3.940-6
	1250°C	1.940-6	8.991-2	3.376-7	4.176-2	1.780-2	7.495-1	5.637-4	6.947-5	9.923-4	9.930-2	4.950-5
	1500°C	4.386-5	8.984-2	5.575-6	4.207-2	1.688-2	7.484-1	1.548-3	3.158-5	2.700-3	9.812-2	3.050-4
	1253°C†	2.038-6	8.991-2	3.528-7	4.176-2	1.779-2	7.495-1	5.730-4	6.868-5	1.008-3	9.929-2	5.094-5
4.211	1000°C	6.696-2	1.333-1	2.158-2	7.069-2	4.124-2	6.662-1	1.692-7	3.067-10	1.268-10	3.018-14	3.805-9
	1250°C	7.240-2	1.279-1	1.615-2	7.613-2	4.123-2	6.662-1	5.971-6	7.793-9	3.566-8	1.442-10	4.127-7
	1500°C	7.554-2	1.247-1	1.303-2	7.925-2	4.115-2	6.662-1	7.809-5	8.032-8	2.053-6	6.375-8	1.189-5
	1900°C†	7.900-2	1.210-1	1.044-2	8.189-2	3.982-2	6.652-1	1.360-3	1.022-6	1.899-4	5.698-5	5.075-4

* In the data format used for this table, X.XXX-Y is equivalent to X.XXX * 10^{-Y}

† Adiabatic flame temperatures.

addition, thermochemical analysis also predicts that HCl formation is highly favored at Herbicide Orange incineration temperatures (1000°C to 1500°C range), and that Cl_2, Cl, ClO and HOCl are found in only trace quantities. The HCl concentrations to be expected from the incineration of Herbicide Orange are in the 1.6 to 2.4 mole percent range.

It may be noted from Table D-2 that the equilibrium CO concentration can be as high as 2800 ppm at 1841°C when the oxygen concentration is 2.8 mole percent. The high equilibrium CO concentration under excess air conditions results from the equilibration of CO_2 according to the water gas shift reaction:

$$CO_2 + H_2 \rightleftharpoons CO + H_2O$$

Since the water gas shift reaction is known to be a relatively slow reaction, the CO_2 equilibration process may not be complete in the incinerator environment, and the actual CO concentration at high incineration temperatures may be considerably lower than the equilibrium CO concentration. It may also be noted from Table D-2 that at air/Herbicide Orange feed ratios between 7.88 and 10.56, and incineration temperatures between 1000°C and 1500°C (the recommended operating region for the destruction of Herbicide Orange, as will be discussed in Section D-2), the maximum equilibrium CO concentration is 72 ppm. At 99.9% combustion efficiency, the allowable CO concentration is 118 ppm (since the CO_2 concentration is 11.8 mole %). Thus the stipulation of a 99.9% combustion efficiency is not limited by equilibrium CO concentrations in the recommended operating region for the destruction of Herbicide Orange.

Adiabatic Flame Temperature

The adiabatic flame temperature is the highest attainable flame temperature when Herbicide Orange is burned in air without loss of heat. The actual flame temperature, depending on the construction of the burner and combustion chamber and heat losses, would be of the order of a hundred degrees lower than the adiabatic flame temperature. For Herbicide Orange, the adiabatic flame temperatures were calculated at four air/waste ratios by using the TRW Chemical Analysis Program, a heat of formation of -152,000 cal/g mole for the normal butyl ester of 2,4-D, and a heat of formation of -159,000 cal/g mole for the normal butyl ester of 2,4,5-T. The results of these calculations are presented in Table D-3, and indicate that the adiabatic flame temperature would be between 1568 and 1253°C (corresponding to an estimated actual flame temperature of 1470 to 1150°C) when the oxygen level in the product gas is between 6.3 and 9.9 mole percent and the air to Herbicide Orange feed ratio is between 7.9 and 10.6 M^3 air/kg Herbicide Orange.

In Figure D-1, the calculated adiabatic flame temperatures are presented as a function of the air to Herbicide Orange feed ratio. It may be noted that the adiabatic flame temperature can be as high as 1900°C under oxygen deficient conditions, and hence temperature control alone is inadequate to ensure complete combustion.

2. ESTIMATION OF EMISSION LEVELS

The thermochemical analysis discussed in the previous section provides information on the equilibrium product distribution from the incineration of Herbicide Orange. These thermochemical calculations, however, cannot be used to estimate the emission levels of 2,4-D, 2,4,5-T or TCDD. The free energies of 2,4-D, 2,4,5-T or TCDD are considerably higher than the free energies

TABLE D-3. ADIABATIC FLAME TEMPERATURE OF HERBICIDE ORANGE AS A FUNCTION OF AIR/HERBICIDE ORANGE FEED RATIO

Air/Orange Ratio $\frac{M^3\ \text{Air}}{\text{kg Orange}}$	Adiabatic Flame Temperature
4.211	1900°C
6.235	1841°C
7.876	1568°C
10.560	1253°C

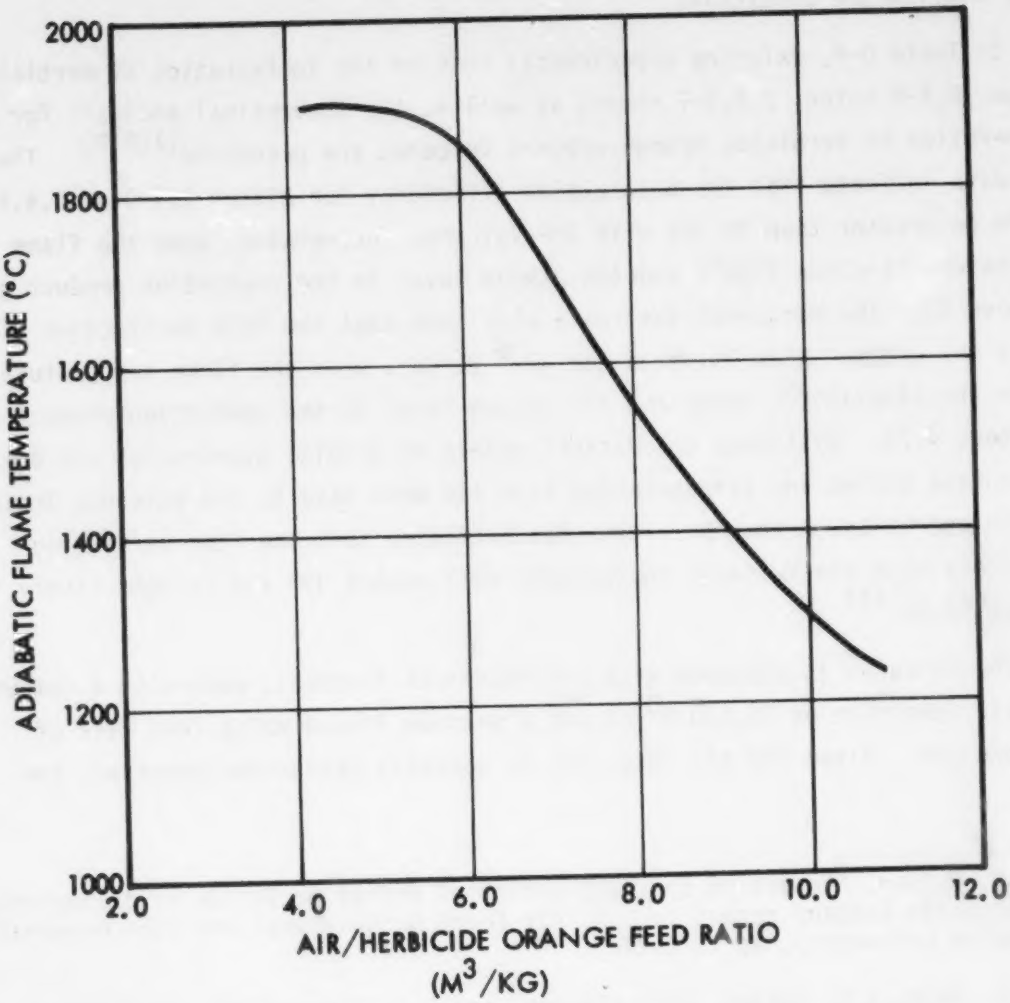

Figure D-1. Adiabatic flame temperature of Herbicide Orange as a function of air/Herbicide Orange feed ratio.

of the stable combustion products CO_2, H_2O and HCl, and none of the Herbicide Orange constituents can theoretically exist in the incinerator environment under equilibrium conditions.

In Table D-4, existing experimental data on the incineration of Herbicide Orange, 2,4-D ester, 2,4,5-T ester, as well as the theoretical analysis for the incineration of Herbicide Orange onboard Vulcanus are presented(1,2,3). The test data indicate that the destruction efficiency for either 2,4-D or 2,4,5-T should be greater than 99.99% with the Vulcanus incinerator, when the flame temperature is above 1000°C and the oxygen level in the combustion product gas is above 5%. The Marquardt test data also show that the TCDD destruction efficiency was greater than 99.9% in the Sue® burner, when the flame temperature was in the 1450-1850°C range and the oxygen level in the combustion product gas was above 4.7%. Utilizing theoretical models of droplet evaporation and combustion gas mixing and extrapolating from the data base to the Vulcanus incineration operation, Arthur D. Little has estimated that the TCDD destruction efficiency with the Vulcanus incinerator will exceed 99% and is most likely to be near 99.9%.(4)

The Vulcanus is equipped with two identical furnaces, each with a combustion air feed rate of 75,000 m^3/hr and a maximum liquid waste feed rate of 12 tonnes/hr. Since the air feed rate is normally maintained constant, the

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1. J.E. Hutson, "Report on the Destruction of Orange Herbicide by Incineration," Marquardt Company report to U.S. Air Force Occupational and Environmental Health Laboratory, April 1974.

2. C.C. Shih, R.F. Tobias, J.F. Clausen, and R.J. Johnson, "Thermal Degradation of Military Standard Pesticide Formulations," TRW Systems and Energy report to U.S. Army Medical Research and Development Command, Report No. 24768-6019-RU-00, March 1975.

3. "Review of Proposed Action to Dispose of Orange Herbicide by Incineration," Report prepared by Arthur D. Little, Inc., for U.S. Air Force occupational and Environmental Health Laboratory, June 1975.

4. B.J. Stojanovic, M.V. Kennedy, and W.C. Shaw, "Thermal Decomposition of Orange Herbicides," Mississippi State University and U.S. Department of Agriculture, June 1972.

TABLE D-4. INCINERATOR DESTRUCTION EFFICIENCY FOR CHLORINATED HYDROCARBONS AND HERBICIDE ORANGE

Test Organization	Test Date	Incinerator	Herbicide Feed Rate	Injection Equipment	Temperature	O_2 Conc. in Stack Gas	Residence Time	Material Burned	Combustion Efficiency	% Destruction Efficiency				
										HC	Chlorinated HC	2, 4-D	2, 4, 5-T	TCDD
Marquardt/USAFEHL	Nov. 1973	Sue Burner	240 kg/hr	Spray Atomizer	1450 - 1750°C	6.6 - 9.7%	0.14 - 0.16 sec	Herbicide Orange	-	99.6 - 99.99	-	>99.999	>99.999	>99.96
Marquardt/USAFEHL	Nov. 1973	Sue Burner	270 kg/hr	Slot Nozzle	1680 - 1860°C	4.7 - 4.9%	0.14 - 0.18 sec	Herbicide Orange	-	99.84 - 99.96	-	>99.999	>99.999	>99.92
TRW	Aug. 1974	Pesticide Incinerator	4.3 kg/hr	Air Assisted Radial Spray	~1000°C	6.7%	0.6 sec	2, 4-D Ester	99.9915*	>99.99	-	99.9995	-	-
TRW	Aug. 1974	Pesticide Incinerator	4.5 kg/hr	Air Assisted Radial Spray	~ 975°C	6.8%	0.65 sec	2, 4, 5-T Ester	99.97981*	>99.99	-	-	99.9995	-
TRW	Aug. 1974	Pesticide Incinerator	3.6 kg/hr	Air Assisted Radial Spray	~1120°C	7.2%	0.45 sec	2, 4-D Ester 2,4, 5-T Ester and No. 2 Oil (1:1:6 Volume Ratio)	99.99051*	>99.99	-	99.9992	99.9992	-
Arthur D. Little Theoretical Analysis	1975	Vulcanus	11.5 tonnes/hr	Rotary Cup	1350°C	7.4%	0.61 sec	Herbicide Orange	-	99.97	-	>99.97	>99.97	>99%†

* Combustion efficiency is defined as (CO_2 concentration - CO concentration) x 100/CO_2 concentration.

† Most likely to be near the 99.9% level.

Note: Percent destruction efficiencies are expressed as >99.9% or >99.999% when the amount of the chemical species found in the combustion product gas is below the detection limit for the species.

maximum liquid waste rate of 12 tonnes/hr stipulates a minimum air/Herbicide Orange feed ratio of 6.25 m^3 air per kg of Herbicide Orange. It has been pointed out that this minimum air/Herbicide Orange feed ratio corresponds to an estimated flame temperature of 1840°C and oxygen level of 3.0% in the combustion product gas. At higher air/Herbicide Orange feed ratios, the estimated flame temperature decreases and the oxygen level in the combustion product gas increases. At an air/Herbicide Orange feed ratio of 10.56 m^3 air per kg of Herbicide Orange, the estimated flame temperature is 1150°C and the oxygen level in the combustion product gas is approximately 9.9%. Since a minimum temperature of 1000°C is necessary to ensure the near complete destruction of TCDD,(4) air/Herbicide Orange feed ratios exceeding 10.56 m^3 air per kg of Herbicide Orange should not be considered for Herbicide Orange incineration. At an air feed rate of 75,000 m^3/hr, the recommended Herbicide Orange feed rate to each Vulcanus incinerator is 7.1 to 9.6 tonnes/hr. The higher Herbicide Orange feed rate is the preferred mode of operation because the resulting higher flame temperature would lead to more rapid evaporation of the liquid herbicide droplets as well as faster chemical reaction rates.

In Table D-5, the estimated emission rates and concentrations for 2,4-D, 2,4,5-T and TCDD from Herbicide Orange incineration on Vulcanus are presented. The 2,4-D and 2,4,5-T emission rates were estimated on the basis of 99.99% destruction efficiency for these herbicide components. The TCDD emission rates were estimated at both 99 and 99.9% destruction efficiency, for TCDD concentrations of 2 to 47 ppmw in Herbicide Orange. As shown in Table D-5, the estimated TCDD concentration in the incinerator effluent is in the 0.14 to 4.23 ppb range at 99% destruction efficiency, and the estimated 2,4-D or 2,4,5-T concentration in the incinerator effluent is 350 to 520 ppb.

In summary, the analysis of existing test data and the theoretical analysis performed by Arthur D. Little have shown that the TCDD present in Herbicide Orange can be successfully destroyed with the Vulcanus incinerator. The best estimate for the TCDD destruction efficiency is 99.9%. To assure high TCDD destruction efficiencies, combustion efficiencies in excess of 99.9% are deemed necessary as an indication that there is adequate mixing between combustibles and air and the combustion process is complete.

TABLE D-5. ESTIMATED EMISSION RATES AND CONCENTRATIONS FOR HERBICIDE ORANGE DESTRUCTION AT TWO AIR/HERBICIDE ORANGE FEED RATIOS

Air Feed Rate (m^3/hr)	Herbicide Orange Feed Rate (tonnes/hr)	Estimated Flame Temperature	O_2 Level in Comb. Product	Emission Rate (g/hr)				Emission Concentration			
				2,4-D	2,4,5-T	TCDD at 99% D.E.	TCDD at 99.9T D.E.	2,4-D	2,4,5-T	TCDD at 99% D.E.	TCDD at 99.9% D.E.
75,000	9.522	~1470°C	~ 6.5%	476	476	0.19-4.47	0.019-0.447	520 ppb	460 ppb	0.18-4.23 ppb	0.018-0.423 ppb
75,000	7.102	~1150°C	~10.0%	355	355	0.14-3.34	0.014-0.334	400 ppb	350 ppb	0.14-3.21 ppb	0.014-0.321 ppb

Note: Estimated flame temperature is assumed to be 100°C lower than the calculated adiabatic flame temperature. The 2,4-D and 2,4,5-T emission rates are based on 99.99% destruction efficiency of these herbicide components. The lower range of estimated TCDD emissions corresponds to a 2 ppmw of TCDD in Herbicide Orange, and the upper range corresponds to a 47 ppmw of TCDD in Herbicide Orange.

APPENDIX E

TRAPPING EFFICIENCY STUDY OF THE LEAR-SIEGLER TRAIN SORBENT TRAP

APPENDIX E

1. INTRODUCTION

The Lear-Siegler sorbent trap system was used in the Herbicide Orange program for two purposes. First, this sampling train was intended to acquire combustion effluent samples for the purposes of assessing the emission burden from the incineration. Secondly, the Lear-Siegler train was intended as a back-up to the primary USAF-OEHL train for measurement of TCDD emissions. Since the Lear-Siegler train had not been used to trap TCDD before this program, it was required to test the trapping efficiency of the system.

2. TEST APPARATUS

A schematic of the test apparatus is shown in Figure E-1. The apparatus consisted of a tube furnace with a special designed tubular glass chamber which extended beyond both ends of the furnace. Specially designed glass boats for containing test samples could be placed in the center of the glass chamber. A thermocouple was placed directly over the glass boat.

The exit end of the glass chamber was connected to an all-glass sampling train consisting of the following parts in series:

- The Lear-Siegler sorbent trap
- Two benzene filled impingers
- One empty impinger
- One activated charcoal filled impinger
- One silica gell filled impinger

The last impinger was connected to a vacuum pump in order to maintain a slight negative pressure in the entire system. The glass tubing between exit end of the chamber and the sorbent trap was wrapped in heating tape and maintained at 190^{0}C.

The upstream end of the glass chamber was connected to a nitrogen cylinder. With a rotameter and needle valve, a constant nitrogen flow through the system

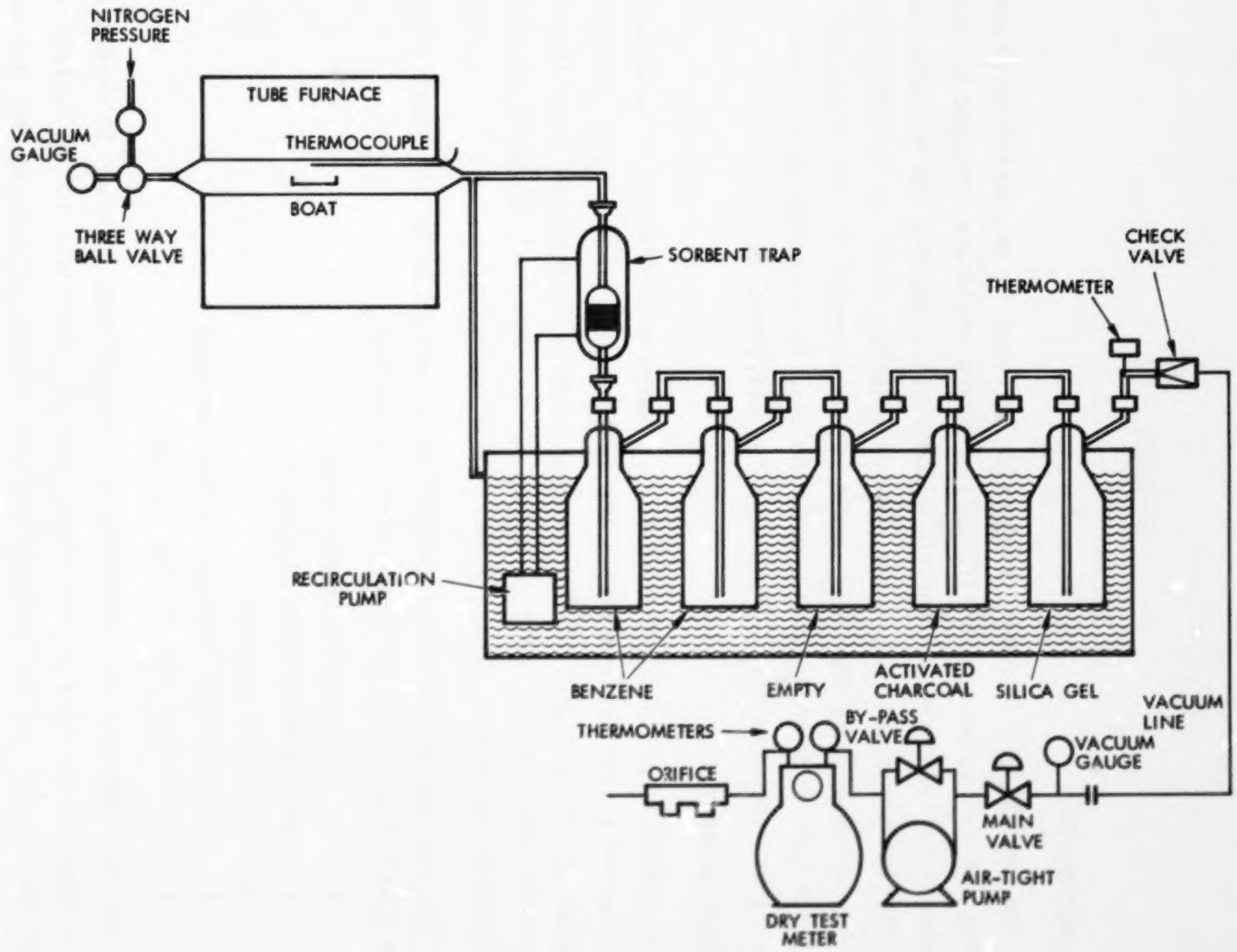
NITROGEN PRESSURE
VACUUM GAUGE
THREE WAY BALL VALVE
TUBE FURNACE
THERMOCOUPLE
BOAT
SORBENT TRAP
CHECK VALVE
THERMOMETER
RECIRCULATION PUMP
BENZENE
EMPTY
ACTIVATED CHARCOAL
SILICA GEL
VACUUM LINE
THERMOMETERS
BY-PASS VALVE
VACUUM GAUGE
ORIFICE
MAIN VALVE
AIR-TIGHT PUMP
DRY TEST METER

Figure E-1. Schematic for sorbent trap efficiency test.

could be maintained. All glass parts outside the tube furnace were wrapped with aluminum foil to prevent degradation of the 2,3,7,8-TCDD (TCDD) samples by uv radiation.

3. PROCEDURE

The procedure was the same for all tests. The apparatus was first leak tested. The sample was added to the glass boat which was then moved to the center of the furnace. The nitrogen purge was started at the same time as the vacuum pump. The flow rate was adjusted to 0.5 liters per minute, and the vacuum was adjusted to maintain an interior pressure of 14 psia. The furnace was then turned on and maintained at $100^{o}C$ for 30 minutes to evaporate the benzene solvent. Then the oven was brought slowly to $400^{o}C$, at which temperature it was kept for 2 hours. The system was then allowed to cool under the nitrogen purge. After cooling, it was disassembled for sample recovery.

Four tests were performed. The first test was a blank in which benzene alone rather than TCDD standards were used. In the second test, 30 μg of TCDD were used. In the third and fourth tests, 60 μg of TCDD were used.

4. SAMPLE RECOVERY

The sample boat was placed in an amber colored glass bottle containing 100 ml of pentane and allowed to soak for 30 minutes. The boat was removed and rinsed into the bottle. The glass chamber and connecting line to the inlet of the sorbent trap were filled with pentane and allowed to stand for 5 minutes. This wash was collected. The chamber and lines were rinsed with additional pentane. The washes and rinses of the boat, chamber, and connecting line were combined as one sample.

Each of the two benzene impingers downstream of the sorbent trap was treated as a separate sample. The benzene contents were recovered. Each impinger was rinsed with benzene, and the rinsings were combined with the recovered contents.

The sorbent trap resin was extracted with pentane in a soxhlet apparatus using standard procedures described in detail in Appendix C. After the resin was removed from the trap, the trap interior was rinsed with pentane, and these rinses were added to the extraction flask. An extraction blank was prepared in an identical manner.

The samples from the tests (sorbent trap extract, the apparatus rinses, and the two benzene impingers) were reduced in volume to 2 ml using Kuderna-Danish concentrators.

5. ANALYSIS

The concentrated samples (and blanks) from the tests were analyzed using a Finnigan 4000 gas chromatograph-mass spectrometer. The analytical and operating parameters were similar to these recommended by WSU(6) and were as follows:

- GC column: 6-ft X 2-mm ID glass column, 3% OV-101 on 100/120 mesh Gas Chrom Q ^{R}
- Carrier gas: helium at 50 ml/min
- Column temperature: 180°C
- Injector: 300°
- Jet separator: 275°C
- Filament current: 0.2 mA
- Multiplier voltage: 200V
- Analyzer pressure: 1-3 X 10^{-6} torr

The m/e 322 ion was monitored and used for quantitation. Calibration standards were the same as used for the tests.

6. RESULTS AND CONCLUSIONS

The results of the analyses are given in Table E-1. On the basis of these results an average minimum efficiency of the sorbent trap for collecting and releasing TCDD is calculated to be 62%.

In a report by A.D. Little, Inc.,(3) the sorbent trap was tested by adding TCDD standards directly into the sorbent resin rather than by vaporizing the TCDD and passing the vapor into the trap. Their average recovery was 65%.

TABLE E-1. RESULTS OF EFFICIENCY STUDY OF THE LEAR-SIEGLER SORBENT TRAP

Test	Sample	μg TCDD	μg TCDD Taken	% TCDD Found
1	Boat, Lines	ND		
	Sorbent Trap	ND		
	Impinger #1	ND		
	Impinger #2	ND		
	Total	<0.1	0.0	0.0
2	Boat, Lines	ND		
	Sorbent Trap	20		67
	Impinger #1	ND		
	Impinger #2	ND		
	Total	20	30	67
3	Boat, Lines	ND		
	Sorbent Trap	44		73
	Impinger #1	ND		
	Impinger #2	ND		
	Total	44	60	73
4	Boat, Lines	ND		
	Sorbent Trap	27		45
	Impinger #1	ND		
	Impinger #2	ND		
	Total	27	60	45

ND indicates not detected.

The similarity of these results leads to the conclusion that the sorbent trap is probably nearly 100% efficient at trapping TCDD but is 62-65% efficient at releasing trapped TCDD by soxhlet extraction.

APPENDIX F

SAMPLE CALCULATIONS

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APPENDIX F

1. PROBE AND LINE RINSE APPORTIONMENT

For the test of 7/16/77, the Lear-Siegler train sampled 6.0914 m^3. The benzene impinger train took three samples, one for WSU of 0.1179 m^3, one for TRW of 0.1209 m^3, and one for BCL/USAF of 0.1211 m^3. These four samples totaled 6.4513 m^3. Each sample represents the following fraction of the total.

- Lear-Siegler - 94.42%
- WSU impinger - 1.83%
- TRW impinger - 1.87%
- BCL/USAF impinger - 1.88%

To apportion the line rinses properly to each sample, the total line rinse volume of 2320 ml was multiplied by the fraction of gas taken in each sample. Thus, 94.42% of 2320 ml is 2191 ml.

The probe rinse split was complicated by the fact that three days of testing were performed before rinsing the probe. Thus 330 ml of probe rinse was obtained and a total of 17.2883 m^3 of gas had been sampled (tests of 14, 15, and 16 July). The Lear-Siegler train sample of 7/16 was 6.0914 m^3 or 35.23% of 17.2883 m^3, and 35.23% of the 330 ml probe rinse was 116 ml.

2. CALCULATIONS FROM GAS COMPOSITION DATA

2.1 Volume Percent HCl in Combustion Effluent

From the data given in Table 13 for test day 2, the volume percent HCl is

$$\text{Vol \% HCl} = \frac{\text{\% Cl/mol wt Cl}}{\text{wt \% Cl mol wt C}} \times \text{Vol \% } CO_2$$

$$= (29.87/35.453)/(49.11/12.011) \times 10.7$$

$$= 2.20\%$$

2.2 Percent Combustion Efficiency

From the data given in Table 13 for test day 2, the percent combustion efficiency, % CE, is

$$\begin{aligned} \% \text{ CE} &= 100\ (\%\ CO_2 - \%\ CO)/\%\ CO_2 \\ &= 100\ (10.7 - 0.0005)/10.7 \\ &= 99.995\% \end{aligned}$$

2.3 Percent Excess Air – EPA Method 3

From data given in Table 13 for test day 2, the percent excess air, % EA, in the combustion effluent is

$$\begin{aligned} \% \text{ EA} &= 100\ (\%\ O_2 - 0.5\%\ CO)/(0.264\%\ N_2 - (\%\ O_2 - 0.5\%\ CO)) \\ &= 100\ (8.1 - 0.5\ (0.0005)/(0.264 \times 79.0 - (8.1 - 0.5\ (0.0005))) \\ &= 63.496\% \end{aligned}$$

3. CALCULATION OF STACK GAS COMPONENT EMISSIONS

3.1 Volumes of Components Emitted Per Metric Ton of Herbicide

The following definitions are used:

C = Weight fraction carbon in herbicide, 0.4911
Cl = Weight fraction chlorine in herbicide, 0.2987
O = Weight fraction oxygen in herbicide, 0.1637
H = Weight fraction hydrogen in herbicide, 0.0465
mt = Metric ton
EA = Excess air

- $V(CO_2) = (C/12.011) \times 10^6$ g/mt $\times$ 0.02406 m^3/mole at 20^oC
  $V(CO_2) = 983.5\ m^3/mt$ at 20^oC, or $916.4\ m^3/mt$ at 0^oC
- $V(HCl) = (Cl/35.453) \times 10^6$ g/mt $\times$ 0.02406 m^3/mole at 20^oC
  $V(HCl) = 202.7\ m^3/mt$ at 20^oC, or $188.8\ m^3/mt$ at 0^oC
- $V(O_2) = V(CO_2) \times \%\ O_2/\%\ CO_2$
  $V(O_2) = 983.5\ (\%\ O_2/\%\ CO_2)\ m^3/mt$ at 20^oC, or
  $916.4\ (\%\ O_2/\%\ CO_2)\ m^3/mt$ at 0^oC

- $V(N_2) = \left(\frac{C}{12.011} + \frac{1}{4}\left(\frac{H}{1.008} - \frac{Cl}{35.453}\right) - \frac{O}{32}\right) \times 10^6$ g/mt x

  0.02406 m^3/mole x (0.7809/0.2095) (1+ EA) m^3/mt at 20^oC
- $V(N_2)$ = 3984 (1 + EA) m^3/mt at 20^oC, or 3712 (1 + EA) m^3/mt at 0^oC
- $V(H_2O$, combustion)

  = (1/2) (H/1.008 - Cl/35.453) x 10^6 g/mt x 0.02406 m^3/mole at 20^oC

  = 453.5 m^3/mt at 20^oC, or 422.6 m^3/mt at 0^oC
- $V(H_2O$, air)

  = $(V(N_2)/0.7809)$ $(P_{H_2O}/760$ mm)

  A typical ambient temperature was 80^oF (26.7^oC), and a typical relative humidity was 84%. Under these conditions, P_{H_2O} was 22.04 mm.

  $V(H_2O$, air)

  = 0.0372 $V(N_2)$

3.2 Volume Rates of Emission

Using averages for all three burns (% O_2 = 8.9, % CO_2 = 10.3, excess air = 74%, feed rate = 7.3 metric tons per hour), the following average volume flow rates at 0^oC were calculated:

- $V(CO_2)$ = 916.4 m^3/mt x 7.3 mt/hr = 6.690 m^3/hr
- V(HCl) = 188.8 m^3/mt x 7.3 mt/hr = 1,378 m^3/hr
- $V(O_2)$ = $V(CO_2)$ x (8.9% O_2/10.3% CO_2) x 7.3 mt/hr = 5,781 m^3/hr
- $V(N_2)$ = 3,712 (1 + 0.74) m^3/mt x 7.3 mt/hr = 47,150 m^3/hr
- $V(H_2O$, combustion)

  = 422.6 m^3/mt x 7.3 mt/hr = 3,085 m^3/hr
- $V(H_2O$, air)

  = 0.0372 $V(N_2)$ = 1,745 m^3/hr

The total average combustion effluent flow rate per incinerator was 65,838 m^3/hr.

4. INCINERATOR RESIDENCE TIME

$$t = \frac{\text{furnace volume}}{\text{emission rate x T/273.16}}$$

The furnace volume was 120 m^3, the average emission rate was calculated to be 65,838 m^3/hr, and the average flame temperature, T, was 1500°C (1773°K). Therefore, the average incinerator residence time for all three burns was

$$t = \frac{120 \text{ m}^3}{\frac{65,838 \text{ m}^3/\text{hr}}{3600 \text{ sec/hr}} \cdot \frac{1773^\circ\text{K}}{273^\circ\text{K}}} = 1.01 \text{ sec}$$

5. GRAVIMETRIC ANALYSES

For sample HO-1-ST-714-F, the pentane extract was made to 300 ml. A 2-ml aliquot was taken for the C7-C16 GC analysis, the remaining 298 ml volume was concentrated to 2 ml. A 0.5 ml aliquot of the concentrate was used for the gravimetric analysis, and a residue weight of 0.561 mg was obtained. A 300-ml aliquot of pentane gave a nonvolatile residue weight of 0.422 mg

$$0.561 \text{ mg} \times 2 \text{ ml}/0.5 \text{ ml} \times 300 \text{ ml}/298 \text{ ml} - 0.422 \text{ mg} = 1.837 \text{ mg residue}$$

6. VOLATILE HYDROCARBON EMISSIONS

A 2-ml aliquot of the line rinse of 7/14/77 was taken for the C7-C16 GC analysis. The volume of line rinse attributable to the Lear-Siegler train sample was 2098 ml. The analysis of this sample indicated a concentration of 14 ng/μl of species in the C8 boiling point range

$$14 \text{ ng}/\mu\text{l} \times 10^3 \mu\text{l/ml} \times 2098 \text{ ml} \times (1/6.2012 \text{ m}^3) \times 10^{-6} \text{ mg/ng} = 7.5 \text{ mg/m}^3$$

7. GC/MS ANALYSES OF LEAR-SIEGLER TRAIN SAMPLES

In the sample HO-1-ST-716-H, dichlorobiphenyl was detected at 10 ng/μl. The volume of this sorbent trap extract was 350 ml, of which 348 ml were concentrated to 2 ml (Table 25). GC/MS analysis was performed on the concentrate. The volume of gas sampled by that sorbent trap was 6.0914 m^3 (Table 6). The emission concentration of dichlorobiphenyl was

$$10 \text{ ng}/\mu\text{l} \times 10^3 \mu\text{l/ml} \times 10^{-3} \mu\text{g/ng} \times 2 \text{ ml} \times 350 \text{ ml}/348 \text{ ml} \times 1/6.0914 \text{ m}^3$$

$$= 3 \mu\text{g/m}^3$$

8. EMISSION CONCENTRATIONS OF 2,4-D, 2,4,5-T, AND TCDD AT 0% DESTRUCTION EFFICIENCY

For the test of 7/16/77, the waste feed rate was 7.03 metric tons per hour per incinerator (Table 17). From the on-line monitoring instruments, the concentrations of O_2 and CO_2 were measured (Table 13) at 8.4% and 10.5%, respectively. The effluent flow rate was calculated to be 60,900 dry m^3/hr at 20^oC from the following equations. Per metric ton of herbicide per hour (Appendix F.3):

$$V_T = V_{CO_2} + V_{HCl} + V_{N_2} + V_{O_2}$$

$$V_{CO_2} = 983.5 \text{ dry } m^3/hr$$

$$V_{HCL} = 202.7 \text{ dry } m^3/hr$$

$$V_{N_2} = 3984 \ (1 + XS \text{ air}) \text{ dry } m^3/hr$$

$$V_{O_2} = V_{CO_2} \times \%\ O_2/\%\ CO_2 = 983.5\%\ O_2/\%\ CO_2 \text{ dry } m^3/hr$$

$$V_T = 60{,}900 \ m^3/hr \text{ at } 20^oC.$$

If the destruction efficiency for 2,4-D + 2,4,5-T were zero, then the emission concentration of 2,4-D + 2,4,5-T would be:

$$7.03 \times 10^3 \text{ kg/hr} \times 10^3 \text{ g/kg} \times (1/60{,}900 \ m^3/hr) = 115 \ g/m^3$$

The TCDD concentration in the composite feed sample of 7/16/77 was determined to be (Table 38) 2.5 µg/ml. If the destruction efficiency for TCDD were zero, then the emission concentration of TCDD would be:

$$7.03 \text{ mt/hr} \times 10^6 \text{ g/mt} \times 2.5 \ \mu g/m\ell \times (1/1.17 \text{ g/m}\ell) \times (1/60{,}900 \ m^3/hr)$$

$$= 247 \ \mu g/m^3$$

The samples of 8/28/77 were acquired while flashing the water in Tank 6P during the third burn (Section 3.2.3). Flashing was performed through the starboard incinerator. The contents of Tank 6P were fed into burner No. 4, and herbicide from other tanks was fed into burners 5 and 6 (see Figure 5). The composite feed sample of 8/28/77 was acquired at burner No. 4, the only burner fitted with a valve for drawing samples. Therefore, this composite feed sample was not representative of the waste being burned during the test. It is necessary to assume a representative composite feed sample in order to determine destruction efficiencies for 2,4-D + 2,4,5-T and TCDD. Details of the assumed representative composite feed are described below.

The composite feed sample of 8/28/77 consisted of two layers. WSU made the following measurements on this sample:

- Top layer - water

1)	specific gravity	1.02 g/cm^3
2)	TCDD concentration	0.77 μg/cm^3
3)	volume percent	70%

- Bottom layer - herbicide

1)	specific gravity	1.2 g/cm^3
2)	TCDD concentration	2.8 μg/cm^3
3)	volume percent	30%

Because feed rates by tank could not be determined during the third burn (Section 4.1.2), the average waste flow rate was used in the calculations. The overall waste feed rate for the third burn was 15.2 metric tons per hour or 2.53 metric tons per burner per hour (6 burners). The specific gravity (Section 4.1.2) was 1.19 g/cm^3, so that the average volume flow rate was 2.13 m^3/hr per burner. Thus, burners 5 and 6 were fed herbicide at an assumed rate of 2.53 metric tons per hour each; and burner 4 was fed a mixture of 70% water and 30% herbicide at an assumed rate of 2.13 cubic meters per hour. From these feed rates and the WSU data above, herbicide and TCDD feed rates can be calculated:

- Burner No. 4

  1) water

     $70\% \times 2.13\ m^3/hr \times 10^6\ cm^3/m^3 \times 1.02\ g/cm^3 \times 10^{-6}\ g/mt$

     $= 1.52\ mt/hr$

  2) herbicide

     $30\% \times 2.13\ m^3/hr \times 10^6\ cm^3/m^3 \times 1.2\ g/cm^3 \times 10^{-6}\ g/mt$

     $= 0.77\ mt/hr$

  3) TCDD, sum of TCDD in water and herbicide

     $70\% \times 2.13\ m^3/hr \times 10^6\ cm^3/m^3 \times 0.77 \times 10^{-6}\ g/cm^3 = 1.15\ g/hr$

     $30\% \times 2.13\ m^3/hr \times 10^6\ cm^3/m^3 \times 2.8 \times 10^{-6}\ g/cm^3 = 1.79\ g/hr$

- Burners 5 and 6

  1) herbicide

     $2 \times 2.53\ mt/hr = 5.06\ mt/hr$

  2) TCDD

     $5.06\ mt/hr \times 10^6\ g/mt \times 2.8 \times 10^{-6}\ g/cm^3 \times 1/1.2\ g/cm^3$

     $= 11.8\ g/hr$

- The total herbicide feed rate is the sum of feeds through burners 4, 5, and 6: 5.83 mt/hr

- The combustion effluent flow rate calculated from the herbicide feed rate of 5.83 mt/hr is 51,900 m^3/hr (20°C)

- The emission concentration at 0% destruction efficiency of 2,4-D + 2,4,5-T is 112 g/m^3

- The total TCDD feed rate is the sum of feeds through burners 4, 5, and 6: 14.7 g/hr

- The emission concentration at 0% destruction efficiency of TCDD is 284 $\mu g/m^3$

9. DESTRUCTION EFFICIENCIES FOR TCDD FROM WSU ANALYSES

In the sample of 7/16/77, WSU found no TCDD. The minimum detectable concentrations (MDC) from Table 38 are used to calculate the maximum possible amount of TCDD in the sample:

- Impinger: MDC = 0.68 ng in 725 ml = <0.68 ng
- Line rinse: MDC = 0.045 ng/ml x 42.5 ml = <1.91 ng
- Probe rinse: MDC = 0.086 ng/ml x 2.3 ml = <0.2 ng

The gas volume sampled was 0.1179 m^3. Thus, the emission concentration of TCDD was:

$$<2.79 \text{ ng}/0.1179 \text{ m}^3 = <23.6 \text{ ng/m}^3$$

From Table 49, the emission concentration of TCDD at 0% destruction efficiency was calculated to be 247 μg/m^3. The destruction efficiency for TCDD was thus,

$$(247 \ \mu\text{g/m}^3 - <0.0236 \ \mu\text{g/m}^3)/247 \ \mu\text{g/m}^3 = >0.9999$$

10. DESTRUCTION EFFICIENCIES FOR 2,4-D AND 2,4,5-T FROM LEAR-SIEGLER TRAIN ANALYSES

Destruction efficiencies for the waste or specific waste constituents are based on comparing the input rate to the emission rate. That is,

$$DE_{\text{waste}} = \frac{\text{waste input - waste output}}{\text{waste input}} \times 100$$

An equivalent method was used in this report. Emission concentrations at 0% destruction efficiency were calculated from waste feed rates and combustion effluent flow rates (Table 49). These values were compared with emission concentrations of, for example, 2,4-D and 2,4,5-T calculated from the laboratory analyses.

For the test of 7/16/77, neither 2,4-D nor 2,4,5-T was detected in the sorbent trap, line rinse, or probe rinse samples. Considering the line rinse only, 248 ml of a sample of 2191 ml (Table 25) were concentrated to 2 ml and then analyzed by GC/MS. The GC/MS detection limit was 1 ng/μl. The volume of gas sampled was 6.0914 m^3. The emission concentration of 2,4-D plus 2,4,5-T was

<1 ng/μl x 10^3 μl/ml x 2 ml x 2191 ml/248 ml x (1/6.0914 m^3) x 10^{-3} μg/ng

= <3 μg/m^3.

A similar calculation was performed for the sorbent trap and probe rinse samples of 7/16/77. The total 2,4-D + 2,4,5-T emission concentration in the sample of 7/16/77 was <7 μg/m^3. The calculated emission concentration of 2,4-D + 2,4,5-T at 0% destruction efficiency is (Table 45) 115 g/m^3. The destruction efficiency for 2,4-D + 2,4,5-T was

(115 x 10^6 μg/m^3 - <7 μg/m^3)/175 x 10^6 μg/m^3 = >0.99999993

11. DESTRUCTION EFFICIENCIES FOR 2,4-D AND 2,4,5-T FROM BCL ANALYSES

Neither 2,4-D nor 2,4,5-T was detected in the benzene impinger sample of 7/18/77 (Table 41). The impinger volume was 600 ml, and the volume of gas sampled was 0.1235 m^3 (Table 52). The detection limits for 2,4-D and 2,4,5-T were 0.08 μg/ml and 0.04 μg/ml, respectively, and were used to calculate the maximum possible amounts in the sample:

<0.08 μg/ml x 600 ml x 1/0.1235 m^3 = <390 μg/m^3 2,5-D

<0.04 μ/ml x 600 ml x 1/0.1235 m^3 = <190 μg/m^3 2,4,5-T

Similar calculations were made for the probe and line rinses. The sample set of 7/18/77 was found to contain:

<590 μg/m^3 of 2,4-D + 2,4,5-T.

The emission concentration at 0% destruction efficiency for 2,4-D + 2,4,5-T on 7/18/77 was 120 g/m^3 (Table 49). The destruction efficiency for 2,4-D + 2,4,5-T was,

(120 g/m^3 - <590 μg/m^3)/120 g/m^3 = >0.99999

12. CONVERSION OF CONCENTRATIONS

Emission concentrations in this report are given exclusively in terms of weight per unit volume, e.g., mg/m^3. This form of presentation was used rather than, e.g., ppm, (1) for ease of comparison of measured levels of 2,4-D and 2,4,5-T with the 8 hour TLV of 10 mg/m^3 and (2) because it is necessary to know molecular weight in order to convert to ppm. Conversions of mg/m^3 to ppm, $\mu g/m^3$ to ppb, and ng/m^3 to parts per trillion (ppt) are illustrated below.

Sample HO-1-ST-714-F was found (Table 27) to have 0.23 mg/m^3 of hydrocarbons quantitated as C10 (n-decane, 144 g/mole). The sample gas volumes were corrected to $20^{o}C$, at which temperature one mole of gas occupies 0.02406 m^3. To convert 0.23 mg/m^3 to ppm:

$$0.23\ mg/m^3 \times 10^{-3}\ g/mg \times (1/144\ g/mole) \times 0.02406\ m^3/mole \times 10^6 = 0.038\ ppm$$

Sample HO-1-ST-716 was found (Table 30) to have 3 $\mu g/m^3$ ($20^{o}C$) of dichlorobiphenyl (223.1 g/mole). To convert 3 $\mu g/m^3$ to ppb;

$$3\ \mu g/m^3 \times 10^{-6}\ \mu g/g \times (1/223.1\ g/mole) \times 0.02406\ m^3/mole \times 10^9 = 0.32\ ppb$$

TCDD (322.0 g/mole) was not detected in sample HO-1-BI-716 (Table 50). The detection limit was used to calculate a maximum possible TCDD concentration of <5.8 ng/m^3 ($20^{o}C$). To convert <5.8 ng/m^3 to ppt:

$$<5.8\ ng/m^3 \times 10^{-9}\ ng/g \times (1/322\ g/mole) \times 0.02406\ m^3/mole \times 10^{12}$$

$$= <0.43\ ppt$$

APPENDIX G

ANALYSIS OF VARIANCE OF DESTRUCTION EFFICIENCY CALCULATIONS

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G. ANALYSIS OF VARIANCE OF DESTRUCTION EFFICIENCY CALCULATIONS

The calculation of destruction efficiency (DE) during this program was based on the measurement of oxygen, carbon dioxide, and carbon monoxide in the combustion effluent; the composition and concentrations of waste feed material; and laboratory analyses of combustion effluent samples.

It is shown in the derivation in this appendix that these factors are sufficient to identify the destruction efficiency without the use of oxygen and waste feed rates because the destruction efficiency is a dimensionless ratio. The variance in destruction efficiency was calculated from the variance in the factors above and their effect on the DE calculation.

1. DERIVATION OF VARIANCE OF DESTRUCTION EFFICIENCY

Let:

W = herbicide feed rate to each incinerator, metric tons per hour

A = air feed rate to each incinerator, dry m^3/hr at 20^oC

P = combustion product flow rate from each incinerator, dry m^3/hr at 20^oC

E = % excess air

C = weight % carbon in Herbicide Orange

H = weight % hydrogen in Herbicide Orange

O = weight % oxygen in Herbicide Orange

$C\ell$ = weight % chlorine in Herbicide Orange

S = stoichiometric oxygen requirement for 100 g herbicide, moles

a = weight fraction 2,4-D + 2,4,5-T in herbicide

b = emission concentration of 2,4-D + 2,4,5-T, metric tons/m^3

d = weight fraction TCDD in herbicide

e = emission concentration of TCDD, metric tons/m^3

At high combustion efficiencies, only traces of CO, hydrocarbons, and waste will be present in the combustion effluent and can be ignored as contributors to the combustion effluent flow rate.

The dry volumetric flow rate for W metric tons per hour of herbicide and A m^3 per hour air feed is derived from stoichiometry as follows:

- The moles of combustion product formed (dry basis) are

$$\text{moles product} = \text{moles } CO_2 + \text{moles } HC\ell + \text{moles } O_2 + \text{moles } N_2$$

- The combustion of 100 grams of herbicide will produce

$C/12.011$ moles CO_2

$C\ell/35.453$ moles $HC\ell$

$1/2\ (H/1.008 - C\ell/35.453)$ moles H_2O

- If there are 0/32 moles of oxygen present in the herbicide, then the stoichiometric requirement for oxygen from the air feed is

$$S = C/12.011 + 1/4\ (H/1.008 - C\ell/35.453) - 0/32 \text{ moles})/100 \text{ g herbicide} \quad (1)$$

- If the combustion effluent contains an excess of air Y% over the stoichiometric requirement, the moles of oxygen in the combustion effluent are:

$$S \times Y/100 \text{ moles } O_2/100 \text{ g herbicide} \quad (2)$$

- The nitrogen content of the product gas follows directly from the composition of feed air, i.e.,

$0.7809S/0.2095$ moles N_2 from oxygen requirement

and

$0.7809S\ Y/(0.2095 \times 100)$ moles N_2 present in the excess air or

$$(0.7809S/0.2095)(1 + Y/100) \text{ moles } N_2 \text{ per 100 g herbicide} \quad (3)$$

where 0.7809 and 0.2095 are the fractional composition of N_2 and O_2, respectively, in a standard dry atmosphere.

- On a dry basis, the moles of combustion effluent produced per 100 g herbicide are

$$C/12.011 + C\ell/35.453 + SY/100 + (0.7809S/0.2095)(1 + Y/100) \quad (4)$$

- The stoichiometric air flow requirement per 100 g herbicide is

$$S/0.2095 \text{ moles} = K'$$

Now, one mole of dry gas occupies 0.02406 m^3 at 20°C. The derivation up to this point has been based on 100 g herbicide. A waste feed of W metric tons per hour is $W \times 10^6/100$ or $W \times 10^4$ times greater than 100 g. Thus, the stoichiometric air flow rate requirement in dry m^3/hr for W metric tons per hour of herbicide is:

$$240.6S\ W/0.2095\ m^3/\text{hr at } 20^\circ C \quad (5)$$

- By definition, from Equation (2), the fraction of excess air is

$$Y/100 = \frac{\text{air flow - stoichiometric air flow}}{\text{stoichiometric air flow}}$$

or

$$Y/100 = (A - 240.6S\ W/0.2095)/(240.6S\ W/0.2095)$$

$$Y/100 = (0.2095A/240.6SW) - 1$$

Therefore,

$$1 + Y/100 = 0.2095A/240.6SW$$

- Equation (4) becomes

$$\frac{C}{12.011} + \frac{C\ell}{35.453} + \left(\frac{0.2095A}{240.6SW} -1\right) S + \frac{0.7809S}{0.2095}\left(\frac{0.2095A}{240.6SW}\right) \text{moles/hr}$$

- Thus the total flow of combustion effluent per incinerator in dry moles/hr at 20°C for W metric tons per hour herbicide feed is

$$P = [C/12.011 + C\ell/35.453 + (A/240.6W) - S]\ 10^4W$$

- Substituting for S from Equation (1) and collecting terms

$$P = \left[\frac{A}{240.6W} + \frac{C\ell}{35.453} - \frac{1}{4}\left(\frac{H}{1.008} - \frac{C\ell}{35.453}\right) + \frac{0}{32}\right] 10^4W \qquad (6)$$

$$= A + 240.6W\ (0132 + C\ell/28.362 + H/4.032)\ m^3/hr$$

- Total 2,4-D + 2,4,5-T fed is Wa metric tons/hour
  Total 2,4-D + 2,4,5-T emitted is Pb metric tons/hour
  Total TCDD fed is Wd metric tons/hour
  Total TCDD emitted is Pe metric tons/hour
- The destruction efficiency (DE) for 2,4-D + 2,4,5-T is

$$DE = \frac{Wa - Pb}{Wa} \times 100$$

or

$$DE - \left(1 - \frac{P}{W}\ \frac{b}{a}\right) \times 100 \qquad (7)$$

- From Equation (5), the air feed rate is proportional to the nitrogen content of the combustion effluent, so

$$A = \frac{240.6SW}{0.2095}\left(1 + \frac{Y}{100}\right) \tag{8}$$

- Therefore, from Equations (6) and (8)

$$P/W = \frac{240.6S}{0.2095}\left(1 + \frac{Y}{100}\right) + 240.6\left(\frac{O}{32} + \frac{C\ell}{28.362} - \frac{H}{4.032}\right) \tag{9}$$

- Substituting Equation (9) into Equation (6) gives

$$DE/100 = \left\{1 - \frac{b}{a} \times 240.6\left[\frac{S}{0.2095}\left(1 + \frac{Y}{100}\right) + K\right]\right\} \tag{10}$$

where

$$K = O/32 + C\ell/28.362 - H/4.032$$

- Excess air, Y in Equation (10), is defined as

$$Y = \frac{\%\ O_2 - 0.5\%\ CO}{0.264\%\ N_2 - (\%\ O_2 - 0.5\%\ CO)} \tag{11}$$

Since CO in the combustion effluent is very small (ppm concentrations compared to percent concentrations for O_2 and N_2),

$$Y \cong \%\ O_2/(0.264\%\ N_2 - \%\ O_2) \tag{12}$$

- The percentage of nitrogen can be inferred as the balance of the product stream after O_2 and CO_2 are measured and $HC\ell$ is calculated, i.e.,

$$\%\ N_2 = 100 - \%\ O_2 - \%\ CO_2 - \%\ HC\ell - \%\ CO - \%\ \text{hydrocarbons}$$

Now, CO and hydrocarbons are trace quantitites, so

$$\% \; N_2 \cong 100 - \% \; O_2 - \% \; CO_2 - \% \; HC\ell \tag{13}$$

- The HCℓ content of the combustion effluent can be deduced from the carbon-to-chlorine ratio in the herbicide because all but trace quantities of Cℓ go to HCℓ and all but trace quantities of C go to CO_2 product. Since

$$\% \; HC\ell = (C\ell/C) \; \% \; CO_2$$

then, substituting into Equation (13)

$$\% \; N_2 \cong 100 - \% \; O_2 - (1 + C\ell/C) \; \% \; CO_2 \tag{14}$$

- Therefore, excess air, Y, is obtained from Equations (12) and (14)

$$Y = \% \; O_2/[0.264 \; (100 - \% \; O_2 - (1 + C\ell/C) \; \% \; CO_2) - \% \; O_2] \tag{15}$$

or

$$Y = \% \; O_2/[26.4 - 1.264\% \; O_2 - 0.264 \; (1 + C\ell/C) \; \% \; CO_2] \tag{16}$$

- Substituting into Equation (10) the expression for Y from Equation (16) and the expression for S in Equation (1), gives

$$DE/100 = \left[1 - \frac{240.6b}{a}\left(K' \cdot \left(1 + \frac{\% \; O_2}{100 \; (26.4 - 1.264\% \; O_2 - 0.264 \; (1 + C\ell/C)\% \; CO_2}\right) + K\right)\right] \tag{17}$$

where

$$K' = \frac{(C/12.011 + (1/4) \; (H/1,008 - C\ell/35,453) - O/32}{0,2095}$$

and

$$K = O/32 + C\ell/28.362 - H/4.032$$

- Now, the quantities K and K' can be assumed to be second-order variations related to the herbicide composition because of the similarity in composition of 2,4-D and 2,4,5-T in the waste. They are neglected. Variances in the $C\ell/C$ ratio, used in the % N_2 calculation, Equation (14), are of more concern because of the magnitude of the N_2 content in the combustion effluent. Variance in the $C\ell/C$ ratio must be considered if the herbicide is diluted subsequent to the determination of a (the weight fraction of 2,4-D + 2,4,5-T in herbicide). This is especially true if the diluent is quite different in composition from the herbicide, such as the diesel fuel used to rinse drums and other equipment involved in loading herbicide on the ship.

- Equation (17) is the final expression for the destruction efficiency of 2,4-D + 2,4,5-T. A similar expression results for the destruction efficiency of TCDD by substituting d for a and e for b, where d and e are, respectively, the weight fraction of TCDD in the herbicide and the emission rate of TCDD in the combustion effluent.

- The variation in DE/100 can be approximated in the region of the average values for the variables O_2, CO_2, $C\ell/C$, a, b, d, and e by Taylor's expansion. Thus, for the variance in destruction efficiency for 2,4-D + 2,4,5-T

$$\begin{aligned} V\,(DE/100) = {} & \left(\frac{\partial\,(DE/100)}{\partial a}\right)^2 V(a) + \left(\frac{\partial\,(DE/100)}{\partial b}\right)^2 V(b) \\ & + \left(\frac{\partial\,(DE/100)}{\partial\,(C\ell/C)}\right)^2 V(C\ell/C) + \left(\frac{\partial\,(DE/100)}{\partial\,O_2}\right)^2 V(O_2) \\ & + \left(\frac{\partial\,(DE/100)}{\partial\,CO_2}\right)^2 V(CO_2) \qquad (18) \end{aligned}$$

The variance in destruction efficiency for TCDD is obtained by substituting d for a and e for b in Equation (18).

- Approximate expressions for the partial derivatives in Equation (18) are

$$\frac{\partial\ (DE/100)}{\partial a} = \frac{240.6b}{a^2}$$

$$\left[K'\left(1 + \frac{\%\ O_2}{100\ (26.4 - 1.264\%\ O_2 - 0.264\ (1 + C\ell/C)\ \%\ CO_2}\right) + K\right] \quad (19)$$

$$\frac{\partial\ (DE/100)}{\partial b} = \frac{-240.6}{a}$$

$$\left[K'\left(1 + \frac{\%\ O_2}{100\ (26.4 - 1.264\%\ O_2 - 0.264\ (1 + C\ell/C)\ \%\ CO_2}\right) + K\right] \quad (20)$$

$$\frac{\partial\ (DE/100)}{\partial\ (C\ell/C)} = \frac{-240.6b\ K'\ \%\ O_2\ (0.264\%\ CO_2)}{100a\ (26.4 - 1.264\%\ O_2 - 0.264\ (1 + C\ell/C)\ \%\ CO_2)^2} \quad (21)$$

$$\frac{\partial\ (DE/100)}{\partial\ (\%\ O_2)} = \frac{-240.6b\ K'}{a}$$

$$\times \left[\frac{26.4 \times 100 + 26.4\ (1 + C\ell/C)\ \%\ CO_2}{(1/\%\ O_2)^2\ [(1/\%\ O_2)(26.4 \times 100\ (1 + C\ell/C)\ \%\ CO_2) - 126.4]^2}\right] \quad (22)$$

$$\frac{\partial\ (DE/100)}{\partial\ (\%\ CO_2)} = -\frac{240.6b\ K'\ \%\ O_2\ (0.264\ C\ell/C)}{100a\ (26.4 - 1.264\%\ O_2 - 0.264\ (1 + C\ell/C)\ \%\ CO_2)^2} \quad (23)$$

The variances in d and e are obtained by substituting d for a and e for b in Equations (19) through (23).

- The means and variances of the variables in Equations (19) through (23) are obtained as follows.

1) V(a), variance in weight percent of 2,4-D and 2,4,5-T in herbicide

From data presented in Table 11 giving the composition of four Gulfport lots of herbicide, the mean and standard deviation in the total of 2,4-D and 2,4,5-T in the herbicide were calculated to be

$$\bar{a} = 0.8599\%$$

$$s_a = 0.0547\%$$

2) V(b), variance in emission concentration of 2,4-D and 2,4,5-T

From data presented in Table 51 giving the emission concentrations of 2,4-D and 2,4,5-T calculated from analyses at TRW, the mean and standard deviation emission concentration of 2,4-D + 2,4,5-T were calculated to be

$$\bar{b} = 46.7\ \mu g/m^3 = 46.7 \times 10^{-12} \text{ metric tons}/m^3$$

$$s_b = 72.2\ \mu g/m^3 = 72.2 \times 10^{-12} \text{ metric tons}/m^3$$

3) V(d), variance in TCDD content of herbicide

The mean and standard deviation in TCDD content of the herbicide were calculated from data presented in Table 50.

$$\bar{d} = 1.916 \times 10^{-6}$$

$$s_d = 7{,}238 \times 10^{-7}$$

4) V(e), variance in emission concentration of TCDD

Table 50 presents emission concentrations of TCDD calculated from the WSU analyses. The mean and standard deviation are

$$\bar{e} = 186\ ng/m^3 = 1.86 \times 10^{-13} \text{ metric tons}/m^3$$

$$s_e = 142\ ng/m^3 = 1.42 \times 10^{-13} \text{ metric tons}/m^3$$

5) $V(C\ell/C)$, variance in chlorine-to-carbon ratio in waste

After drums containing herbicide were drained, they were rinsed. During Johnston Island dedrumming operations, drums averaged 50 gallons of herbicide, and drum rinses averaged 2 ±0.3 gallons of diesel fuel. The carbon content of diesel fuel was taken as 84.9% and its specific gravity as 0.778. From Table 8, the carbon and chlorine contents of the herbicide were 49.11 and 29.87%, respectively. From these data, the ±2s range for the Cℓ/C ratio is 0.5798 to 0.5870. Therefore,

$$\overline{C\ell/C} = 0.5834$$

$$s_{C\ell/C} = 0.0018$$

6) $V(O_2)$ variance in oxygen content of combustion effluent

Table 16 presents gas composition data for all three burns. From these data, the average and standard deviation of % O_2 were calculated:

$$\% \overline{O_2} = 8.9$$

$$s_{\% O_2} = 1.4$$

7) $V(CO_2)$, variance in carbon dioxide content of combustion effluent

From data presented in Table 16, the average and standard deviation at % CO_2 were calculated:

$$\% \overline{CO_2} = 10.3$$

$$s_{\% CO_2} = 1.7$$

8) Values for K and K' were obtained from the average herbicide composition. From Table 8,

carbon = 49.11%

chlorine = 29.87%

oxygen = 16.37%

hydrogen = 4.65%

$$K = 16.37/32 + 29.87/28.362 - 4.65/4.032 = 0.4114$$

$$K' = \frac{(49.11/12.011 + 4.65/4.032 - 5.974/28.362 - 16.37/32)}{0.2095}$$

$$= 21.5744$$

- In summary, the values needed to solve Equations (17) through (23) are given in Table 56.

TABLE 56. SUMMARY OF ERROR ANALYSIS VARIANCES

	Variable	Units	Mean	Standard Deviation	$\left[\frac{\partial(DE/100)}{\partial(Variable)}\right]^2$	
					2,4-D+2,4,5-T	TCDD
a	Weight fraction 2,4-D + 2,4,5-T in herbicide	dimensionless	0.8599	0.0547	1.13×10^{-13}	---
b	Emission concentration of 2,4-D + 2,4,5-T	metric ton/m^3	4.67×10^{-11}	7.22×10^{-11}	$3.85\times10^{+7}$	---
d	Weight fraction TCDD in herbicide	dimensionless	1.916×10^{-6}	7.23×10^{-7}	---	$7.30\times10^{+4}$
e	Emission concentration of TCDD	metric ton/m^3	1.859×10^{-13}	1.42×10^{-13}	---	$7.75\times10^{+18}$
Cℓ/C	Chlorine/carbon ratio in waste	dimensionless	0.5834	0.0018	3.36×10^{-19}	1.07×10^{-12}
$\%O_2$	Oxygen content of combustion effluent	percent	8.9	1.4	7.05×10^{-18}	1.12×10^{-22}
$\%CO_2$	Carbon dioxide content of combustion effluent	percent	10.3	1.7	1.38×10^{-21}	3.45×10^{-15}
K	Second order variable	moles	0.4144	---	---	---
K'	Second order variable	moles	21.57	---	---	---

2. MEAN AND VARIANCE OF DESTRUCTION EFFICIENCIES

2.1 2,4-D and 2,4,5-T

- Solving Equation (18) with the values in Table 56, the variance and standard deviation of (DE/100) of 2,4-D + 2,4,5-T are:

$$V\ (DE/100) = 2.009 \times 10^{-13}$$

$$s\ (DE/100) = 4.482 \times 10^{-7}$$

- From Equation (17), the mean destruction efficiency for 2,4-D + 2,4,5-T is

$$\overline{DE}/100 = 0.99999971$$

- It is assumed that calculations of destruction efficiency are normally distributed. The question asked is what percent of a group of destruction efficiency calculations will be less than some specified value and what degree of confidence is there in that estimate of the percentage.

  There are three values for emission rates of 2,4-D + 2,4,5-T given in Table 51. Safety considerations dictate consideration of destruction efficiencies less than some specified value. This value is defined as the one-sided tolerance limit. The value for the one-sided tolerance factor was selected(1) for the population of three analyses such that there would be 95% confidence that not more than 0.1% of 2,4-D + 2,4,5-T destruction efficiencies would be less than the tolerance limit. In other words, the tolerance limit is such that there is 95% confidence that only one 2,4-D + 2,4,5-T destruction efficiency in 1000 would be smaller in value.

  $K = 13.86$, one-sided tolerance factor for
  $n = 3$ at 95% confidence

  The tolerance limit is

  $$\overline{DE}/100 - sK = 0.99999971 - 13.86 \times 4.482 \times 10^{-7}$$
  $$= 0.9999935$$

- Therefore, this conservative statistical analysis shows that there is 95% confidence that not more than 1 measured destruction efficiency in 1000 would be less than 99.99935%.

2.2 TCDD

- Solving Equation (18) with the values in Table 56, the variance and standard deviation of (DE/100) of TCDD are:

  $$V(DE/100) = 1.944 \times 10^{-7}$$
  $$s(DE/100) = 4.409 \times 10^{-4}$$

- From Equation (17) the mean destruction efficiency for TCDD is

  $$DE/100 = 0.99948$$

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1. "Handbook of Statistical Tables," D.B. Owen, Addison-Wesley, New York, p. 117, 1962.

- It is assumed that calculations of destruction efficiency for TCDD are normally distributed. The questions asked is what percentage of a group of dioxin destruction efficiency calculations will be less than some specified value and what degree of confidence is there in that estimate of the percentage.

  There are four values for emission rates of TCDD given in Table 50. Safety considerations dictate consideration of destruction efficiencies less than some specified value. This value is defined by the one-sided tolerance limit. The value for the one-sided tolerance factor was selected(1) for the population of four analyses such that there would be 95% confidence that not more than 0.1% of TCDD destruction efficiencies would be less than the tolerance limit. In other words, the tolerance limit is such that there is 95% confidence that only one TCDD destruction efficiency in 1000 would be smaller in value.

  $K = 9.21$, one-sided tolerance factor for $n = 4$
  at 95% confidence

  The tolerance limit is

  $$\overline{DE}/100 - sK = 0.99948 - 9.21 \times 4.409 \times 10^{-4}$$

  $$= 0.9954$$

- Therefore, this conservative statistical analysis shows that there is 95% confidence that not more than 1 measured destruction efficiency for TCDD in 1000 would be less than 99.54%.